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Storage of Nitrogen in Silicate Minerals and Glasses

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Storage of Nitrogen in Silicate Minerals and Glasses

By

Kristin E. Lazzeri

A Thesis

Presented to the Graduate and Research Committee

of Lehigh University

in Candidacy for the Degree of

Master of Sciences

in

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Thesis is accepted and approved in partial fulfillment of the requirements for the Master of Science in Earth and Environmental Science.

Storage of Nitrogen in Silicate Minerals and Glasses
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ABSTRACT

The processes by which organic nitrogen (N) is incorporated and redistributed within the geosphere are important for understanding modern volatile recycling and longer-term Earth degassing and atmosphere evolution. The N isotope system shows great potential for tracing the transfer of volatiles among Earth's major reservoirs, including the transfer of organic N into solid inorganic phases. In order to fully exploit the N isotope system as a tracer of pathways of organic components into the solid inorganic Earth, numerous high- and low- temperature processes must be examined closer. This research explores part of the biogeochemical cycle, focusing on three separate pathways for the transfer of organic N into solid inorganic phases in the shallow crust and on the sea floor.

Chapter 1 focuses on the potential for the storage of N (i.e., N₂ and possibly also as NH₄⁺) within micropores or channels of the cyclosilicate minerals beryl and cordierite. Nitrogen in these systems is believed to be derived ultimately from the diagenesis of organic matter within low-high metamorphic rocks; however, the N concentrations and isotopic compositions of cyclosilicates in pegmatites obviously could reflect a wide range of metamorphic and igneous processes, including subsolidus devolatilization, partial melting, and later differentiation of melts. In metasedimentary rocks, organic N is transferred into clay minerals and later released into fluids during prograde dehydration reactions and can be incorporated into cyclosilicates during or after formation. For both the metamorphic and the igneous samples examined in this study, isotopic analyses of the N₂ residing in cyclosilicates could help elucidate fluid-rock interactions and could potentially contribute information regarding fluid-mineral fractionation useful in a wider

range of studies employing the N isotope system.

Chapter 2 explores the possibility that measurable amounts of organic N, as N₂, may be incorporated into the cages of low-temperature microporous silica phases. Melanophlogite, a silica clathrasil, was used in this study because it forms in hydrothermal settings and contains cages known to house N₂. The hypothesis tested in this research was whether N₂ in the cages of melanophlogite would be retained at temperatures lower than those of its crystallization (<100°C), and if so, the extent to which the isotopic compositions of this N₂ could provide useful information regarding the source(s) of the N and the fluid-rock processes operating during their formation.

The work presented in Chapter 3 examined the ability of palagonized volcanic glasses to incorporate and retain N likely delivered from pore fluids in altered ocean sediments. The chemical exchange of hydrothermal fluids and/or seawater with oceanic crust leads to changes in the chemical compositions of oceanic crust and is viewed as likely impacting N crust-mantle cycling. Volcanic glasses are easily replaced by hydrous phases such as clays or zeolites and are more susceptible than silicates to microbial alteration. Because volcanic glass alters more readily than silicate minerals, the glass could, for some elements (such as N), contribute more significantly to the overall chemical mass-balance of seafloor alteration and could be an important pathway for geochemical cycling within the Earth, especially when it becomes subducted. This study focused on the N concentrations and isotopic compositions of suites of volcanic glasses showing a spectrum of alteration intensities that have been previously characterized for evidence of microbial alteration. Differences in the N contents and d¹⁵N of unaltered and altered glasses from the same section were compared, leading to some hypotheses

regarding the sources of the N and the timing of incorporation relative to the cooling and degassing the lavas and later lower-temperature alteration.

Chapter 1: Nitrogen Storage in the Cyclosilicates Beryl and Cordierite

ABSTRACT

The N isotope system shows great potential for tracing the transfer of volatiles among Earth's major reservoirs, including the transfer of organic N into solid inorganic phases. This work explored the potential for the storage of N (i.e., N₂ and possibly as ammonium) within the micropores or channels of cyclosilicate minerals. Isotopic analyses of the N₂ residing in these phases could help elucidate fluid-rock interactions, potentially contributing information regarding fluid-mineral fractionation.

This work focused primarily on the N stored in the cyclosilicate minerals beryl and cordierite, and analyses were undertaken of gem-quality samples from igneous and metapelitic rocks from around the globe. Many of the cyclosilicate samples are from well-known localities and have been previously studied in degassing experiments and in investigations of volatile storage. All samples contain measurable quantities of N, presumably in their channels, and $\delta^{15}\text{N}_{\text{air}}$ values are indicative of initially organic origins (0-12‰). Co-existing beryl/cordierite and micas were analyzed in order to investigate isotopic fractionation between fluid N₂ in cyclosilicate channels and structurally bound NH₄⁺ in the micas. In beryl-muscovite pairs, the beryl consistently has lower N concentrations and lower $\delta^{15}\text{N}$ values than the coexisting muscovite. Data for cordierite-biotite pairs show different and somewhat scattered relationships, and some cordierites have higher N concentrations and higher $\delta^{15}\text{N}$ values than the coexisting biotite. Both beryl and cordierite can contain up to ~4500 ppm N, presumably as channel guest molecules, and commonly contain 100's of ppm of N.

This survey of the N (and C) stored in the channels of beryl and cordierite will

serve as a means of focusing future research on this topic. This additional work should concentrate on elucidating N behavior in cyclosilicate-bearing systems through detailed study of individual igneous and metamorphic units from which cyclosilicates can be physically separated. This future work also should investigate the extent to which N incorporated at “peak” temperatures is retained over protracted cooling histories.

INTRODUCTION

The nitrogen (N) isotope system shows the potential to trace the transfer of volatiles among Earth's reservoirs as well as related fluid-rock interactions, including those that result in the incorporation of organic N into solid inorganic phases (Bebout and Fogel, 1992; Bebout, 1997; Jia et al., 2001; Svensen et al., 2008). Nitrogen in sedimentary systems can exist as molecular nitrogen (N_2) or NH_3 in fluids, depending on the oxidation/reduction states of the rocks, or as NH_4^+ substituting for K^+ in clays and micas (Homna and Itihara, 1981; Duit et al., 1986). Because there is an abundance of these phases within the crust, the N isotope system may be a useful tracer of sediment-derived fluids. Diagenesis of organic matter results in the transfer of organic N into clay minerals as NH_4^+ , and during metamorphism this N is released into fluids during prograde dehydration reactions (Hallam and Eugster, 1976; Duit et al., 1986; Haendel et al., 1986; Bebout and Fogel, 1992). Study of partially melted sedimentary rocks indicates that a significant fraction of the initial sedimentary N is retained even in melt residues, perhaps as NH_4^+ in K-feldspar or as N_2 in the channels of cordierite (see Palya et al., 2010), or also in fluid inclusions (Andersen et al. 1990, 1993; Kreulen and Schuiling, 1982; Casquet, 1986; Touret, 2001).

During metamorphism, the fluid phase is typically removed from rocks during devolatilization and melting, making it difficult to directly study the volatile species that were once present. Thus, the fluid composition must be inferred through thermodynamic calculations (see Moine et al., 1994) or study of fluid inclusions entrapped in solid phases during their crystallization (Darimont et al., 1988; Bottrell et al., 1988). A select few minerals, however, can occlude N (as N_2) and other molecular species (particularly H_2O

and CO₂) in microcavities, pores, or channels that may preserve metamorphic fluids during peak pressures and temperatures (see the early work by Scalan, 1958; Damon and Kulp, 1958). The cyclosilicates cordierite and beryl are two minerals that contain these channels and can be directly used for fluid studies if channel-gas compositions at peak metamorphic conditions are preserved (e.g. Vry et al., 1990; Harley, 1994; Carrington and Harley, 1996; Harley and Carrington, 2001; Harley et al., 2002). Therefore, studying these channel volatiles is an important step for eventually interpreting metamorphic assemblages and drawing inferences about metamorphic-fluid compositions. If N concentrations and isotopic signatures of the original fluids are conserved within these channels, N could provide unique details regarding fluid-rock interactions that other stable isotope systems, such as O, H, C, and S, do not record (Bebout, 1997). As an example, the preservation of an organic signature (0-12‰) could be used to trace the passage of sediment-derived volatiles through high temperature crustal processes.

This study was aimed at obtaining a preliminary understanding of the storage of N within the channels of beryl and cordierite. Samples from a variety of petrologic environments were analyzed to determine the ranges of N concentrations and $\delta^{15}\text{N}$ within natural beryl and cordierite. Many of these samples were gem-quality specimens on which Geiger et al. (in press) recently conducted detailed degassing experiments. Isotopic analyses of the N residing in these phases could help elucidate fluid-rock interactions, and could potentially contribute information regarding fluid-mineral fractionation. This fractionation, if recorded, would likely be reflected in higher $\delta^{15}\text{N}$ values for micas (as NH_4^+) than for cyclosilicates (N_2), based on the calculated NH_4^+ - N_2 fractionations of Hanschmann (1981; also see Haendel et al., 1986).

BACKGROUND

Crystal Chemistry and Occurrences of Cyclosilicate Minerals

Cordierite has the idealized composition $(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18} \cdot [\text{H}_2\text{O}, \text{CO}_2, \text{N}_2 \dots]$ and is commonly found in metamorphic and certain igneous rocks (Clarke, 1995), including pegmatites (Heinrich, 1950). In metapelitic rocks, cordierite stability is restricted to relatively low pressures, thus it is abundant only in the shallow- to mid-continental crust (see figure 1.1). Naturally occurring cordierites tend to have a tetrahedral framework structure with (Si,Al)-ordered orthorhombic low-temperature modification (figure 1.2). The crystal-chemical formula of low cordierite can be written as $(\text{M})_2(\text{T}_1)_2(\text{T}_2)_2(\text{T}_3)_2(\text{T}_4)_2(\text{T}_5)_0_{18}, (\text{Ch}_0, \text{Ch}_{1/4})$, where six-membered rings of T_2 tetrahedra are cross-linked into a framework by T_1 tetrahedra. Octahedral M-sites typically contain Mg^{2+} , Fe^{2+} , Mn^{2+} , or Li^+ . Aluminum is ordered on sites T_1 and T_2 , while Si occupies T_3 , T_4 , and, T_5 . Na^+ or K^+ ions can occupy Ch_0 , while molecules like H_2O and CO_2 can be incorporated on $\text{Ch}_{1/4}$ (Gibbs, 1966; Meagher, 1967; Cohen et al., 1977; Meagher and Gibbs, 1977; Hochella et al., 1979; Wallace and Wenk, 1980).

Beryl ($\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$) $\cdot [\text{H}_2\text{O}, \text{CO}_2, \text{N}_2 \dots]$ is typically found in granites/granite pegmatites and sometimes in mafic metamorphic rocks and low- to high-temperature hydrothermal veins. Beryl is isostructural to cordierite, but in contrast to cordierite, the Be and Si tetrahedra in beryl are distinct from one another. The structure consists of stacked six-membered rings of Si tetrahedra parallel to the c axis, cross-linked by Be tetrahedra and Al octahedra to form a three-dimensional framework (Gibbs, 1966). This stacked-ring structure houses structural cavities connected by narrow bottlenecks with a diameter of about 2.8 Å in which large alkali cations such as Na^+ , K^+ , and potentially also

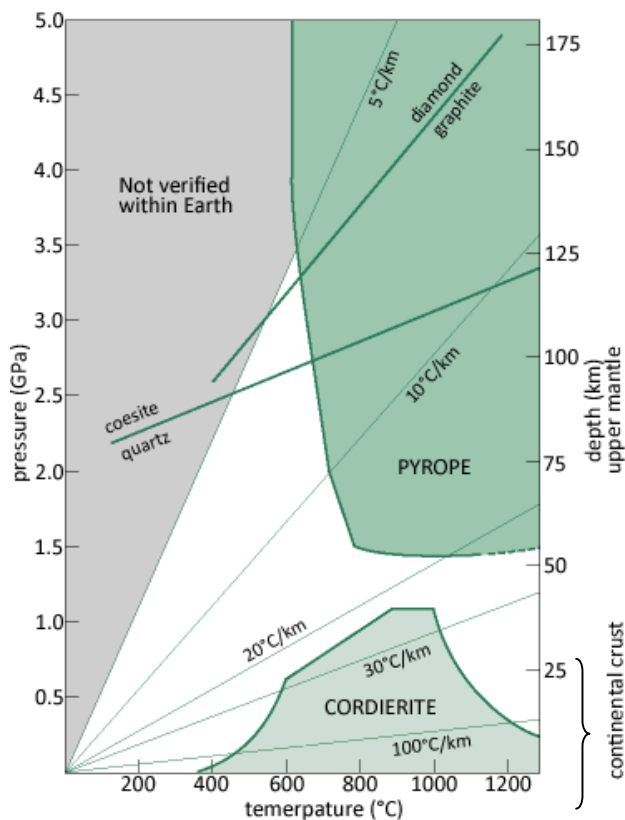


Fig. 1.1 Pressure–temperature plot showing the stability field of cordierite (shaded light blue-grey). Heavy lines indicate the transition conditions for the polymorphs quartz and coesite, and graphite and diamond. From Schreyer (1998).

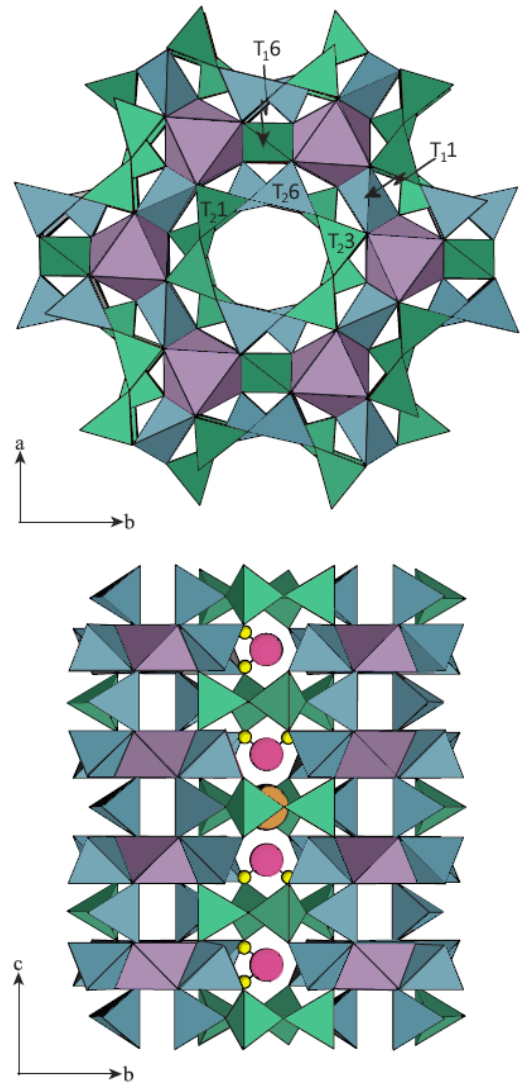


Fig. 1.2 Polyhedral structural model of low cordierite altered from Bertoldi et al. (2004). Si occupies the tetrahedra in green (T_{16} , T_{21} , and T_{23}) and Al those in blue (T_{11} and T_{26}). The large orange sphere represents Na^+ within large spaces of the channels (Ch0-site). The small yellow spheres connected to a pink sphere represent water molecules within the channels. Not pictured are other molecules or neutral tetrahedra atoms that may be present within the channels (CO_2 , N_2 , CO , O_2 , H_2S , Ar, He). Beryl is isostructural to cordierite and will have similar properties.

NH_4^+ can be incorporated (Gibbs, 1966).

Channel Volatiles in Cyclosilicates

Besides cations, beryl and cordierite can incorporate various molecules (H_2O , CO_2 , N_2 , CO , O_2 , and H_2S) and neutral atoms (Ar, He) into their channels (Damon and Kulp, 1958; Wickersheim and Buchanan, 1959; Farrell and Newnham, 1967; Wood and Nassau, 1967, 1968; Beltrame et al., 1976; Langer and Schreyer, 1976; Goldman et al., 1977; Mottana et al., 1983; Aines and Rossman, 1984; Hagemann et al., 1990; Charoy et al., 1996; Kolesov and Geiger, 2000). These volatiles can be incorporated into the channels during crystal formation (Santosh et al., 1993) or “forced in” at very high pressures (Armbruster, 1985). There are kinetic barriers preventing fluid diffusion, potentially allowing the volatiles at these peak conditions to be retained within the channels during cooling and at surface conditions. Channel-ways should be unfavorable for molecular diffusion when the entrapped molecule has a radius greater than 1.235 Å (Geiger et al., in press). For radii greater than this, channel ways can be described as consisting of linked, but separate, micropores that contain occluded molecules. The presence of cations (Na^+ and K^+) within the channels can block diffusion of volatiles from cyclosilicates (Geiger et al., in press).

The dominant channel constituents in natural cyclosilicates are H_2O (up to 3.8 wt %) and CO_2 (up to 2.2 wt %), molecules that have been studied extensively as potential geobarometers and water-fugacity indicators (e.g. Holdaway and Lee, 1977; Zimmermann, 1981; Armbruster, et al., 1982; Vry et al., 1990). Previous analytical studies have shown that increases in temperature cause the total volatile contents in cordierite to decrease, whereas an increase in fluid pressure produced higher total volatile

contents (Schreyer and Yoder, 1964; Mirwald and Schreyer, 1977; Armbruster and Bloss, 1980). It has also been observed that natural cordierites from low-grade metamorphic rocks tend to be more H₂O-rich, whereas cordierites from high-grade granulites tend to be more CO₂-rich (Zimmermann, 1981; Vry et al., 1990; Lepezin et al., 1999). This trend could be explained by either an increase in CO₂ content, low proportion of H₂O, changes in pressure and temperature, or a combination of these. At conditions where fluid is present, the total abundance of channel H₂O and CO₂ is a function of pressure, temperature, and X_{CO2} of the coexisting fluid (Johannes and Schreyer, 1981).

Detection of H₂O and CO₂ within the channels reveals that H₂O molecules occur in two main orientations, I and II, and that the long axis of CO₂ molecules is oriented parallel with the crystallographic a direction (Aines and Rossman, 1964; Goldman et al., 1977). The H-H vector of H₂O I is aligned parallel with the channels c axis whereas the H-H vector of H₂O II is parallel with the crystallographic b axis. H₂O II is assumed to interact with alkali cations that may be present in cordierite channels, which does not seem to be the case for H₂O I. Kolesov and Geiger (2000) additionally identified H₂O with its H-H vector parallel with the crystallographic a, showing no interaction with alkalis. Stopler (1982) observed that H₂O can be incorporated into melts as molecular H₂O and through the breaking of Si-O linkages producing HO- and -OH pairs. Because these fluids behave differently in the wide variety of petrologic environments, it is uncertain how N₂ in fluids in the channels of cyclosilicates will behave with increasing temperatures. If N contents in channels show an inverse correlation with H₂O, N₂ could be incorporated into the space provided in the channels as H₂O is removed.

Degassing experiments reveal that N₂ is the third-most abundant species within

the channels of cyclosilicates, suggesting that N₂ may play an important role in the original fluids (Geiger et al., in press). Nitrogen speciation in fluids is believed to be controlled by the oxygen and water fugacities of the system (Andersen et al., 1993). Fluid inclusion data from granulites and eclogites confirm the presence of N₂-bearing metamorphic fluids at elevated temperatures and pressures (Andersen et al., 1990, 1993; Kreulen and Schuiling, 1982; Touret, 2001). In addition to N₂, several studies have observed the presence of minor amounts of NH₄⁺ and NH₃ within the channels of both cordierite and beryl (Mashkovtsev and Solntsev, 2002; Bul'bak and Shvedenkov, 2005). The abundance and isotopic composition of N incorporated into cordierite and beryl are believed to depend on several factors: (1) the temperature and pressure during crystal growth (petrologic environment), (2) crystal-chemical and molecular properties, (3) the composition of the fluid present when the mineral crystallized, and (4) the fractionation effects of N within fluids. A few studies have investigated whether N₂ is incorporated into cyclosilicates and the possible ranges in N concentrations (Lepezin et al., 1999; Geiger et al., in press), but very few data exist for the N isotopic compositions of N₂ stored in these channels (see the small dataset for beryl presented in Scalan, 1958).

H₂O and CO₂ Partitioning

Experiments investigating the partitioning of volatiles between cordierite and coexisting melts (Carrington and Harley, 1996; Harley et al., 2002) help define whether the channel composition is in equilibrium with the melt or fluid phase. When there is no free volatile phase and melt is present, the absolute abundance of channel H₂O and CO₂ is determined by the partitioning of these molecules between cordierite and melt (Harley, 1994; Stevens et al., 1995; Carrington and Harley, 1996; Harley and Carrington, 2001;

Thompson et al., 2001; Harley et al., 2002). The uptake of H₂O by cordierite coexisting with a melt is controlled by the partitioning coefficient D_w (equation 1.1), which is mainly temperature-dependent (Harley and Carrington, 2001; Harley et al., 2002). Harley and Carrington (2001) found D_w to be highest when cordierite was saturated with H₂O. During an undersaturation of H₂O, D_w exhibited intermediate values and D_w increased as more H₂O was incorporated into the cordierites. CO₂ hardly affects the distribution of H₂O between cordierite and melt (Thompson et al., 2001). Nitrogen could behave similarly to CO₂ in these situations and similar results should be observed in the case of beryl. Partitioning between minerals and fluids depends on water activity and oxygen fugacity during metamorphism (Andersen et al., 1993).

$$D_w = \frac{\text{wt \% H}_2\text{O (melt)}}{\text{wt \% H}_2\text{O (cordierite)}} \quad (1.1)$$

Volatiles and Equilibrium

It is important to establish conditions of equilibrium to confirm the validity of N fractionation between N₂ and NH₄⁺ in these experiments. Many of the studies investigating equilibration have looked at $\delta^{13}\text{C}$ of CO₂ within the channels of cordierite and compared it with $\delta^{13}\text{C}$ in coexisting fluid inclusions or graphite (see Vry et al., 1990). Santosh et al. (1993) analyzed CO₂ from cordierites and fluid inclusions and determined that the CO₂ was incorporated during crystal growth, with little re-equilibration during later influxes. Similar results have been obtained from studies on graphites; channel contents are not significantly affected by retrograde isotope exchange, as it preserves high-temperature carbon fractionation with coexisting graphite (Vry et al., 1990; Fitzsimons and Matthey, 1995). Recent experiments and modeling of the cordierite H₂O-CO₂ saturation surfaces (Thompson et al., 2001; Harley and Carrington, 2001; Harley et

al., 2002) even show equilibrium of volatile contents in cordierite at high X_{CO_2} . If N acts similarly in these systems, we would expect N_2 in the channels of cyclosilicates to be in equilibrium with N in other minerals formed at the same time.

Degassing Experiments

Degassing experiments by Geiger (in press) show the presence of N within the channels for many of the cordierites presented here. In these experiments, cordierites from a wide range of petrologic environments were analyzed using quadrupole mass spectrometry while step heating from 25 to 1400°C. These measurements documented the types of released molecular species and their concentrations as well as the maximum temperatures of gas release for each species. Because this method discriminates volatiles by their mass-to-charge ratios (m/z), N_2 and CO are both observed at m/z 28. N_2 was discriminated from CO by elevated m/z 28:44 ratios, indicating that a peak at m/z 28 cannot be solely explained by secondary CO^+ fragments produced from occluded CO_2 molecules. In order to test for the presence of the occluded N_2 molecule, one can use the species m/z 14, which can be assigned to the fragment N^+ (see figure 1.3, from Geiger et al., in press).

Geiger et al. (in press) observed that the most N_2 -rich samples are those from the granulite facies (7114, VS-1). Cordierites from medium-grade rocks (25-Geco Mine, TA-5, WYO-2) contain less N_2 , and pegmatite samples show the least N_2 (84264, 26230, 88593, G-155a). These results generally confirm the conclusions of Lepezin et al. (1999), showing that the concentration of N_2 in cordierite increases with increasing metamorphic grade; however, they did not observe N in pegmatites. There are some issues with this method as it assumes much regarding how the molecules should speciate within these

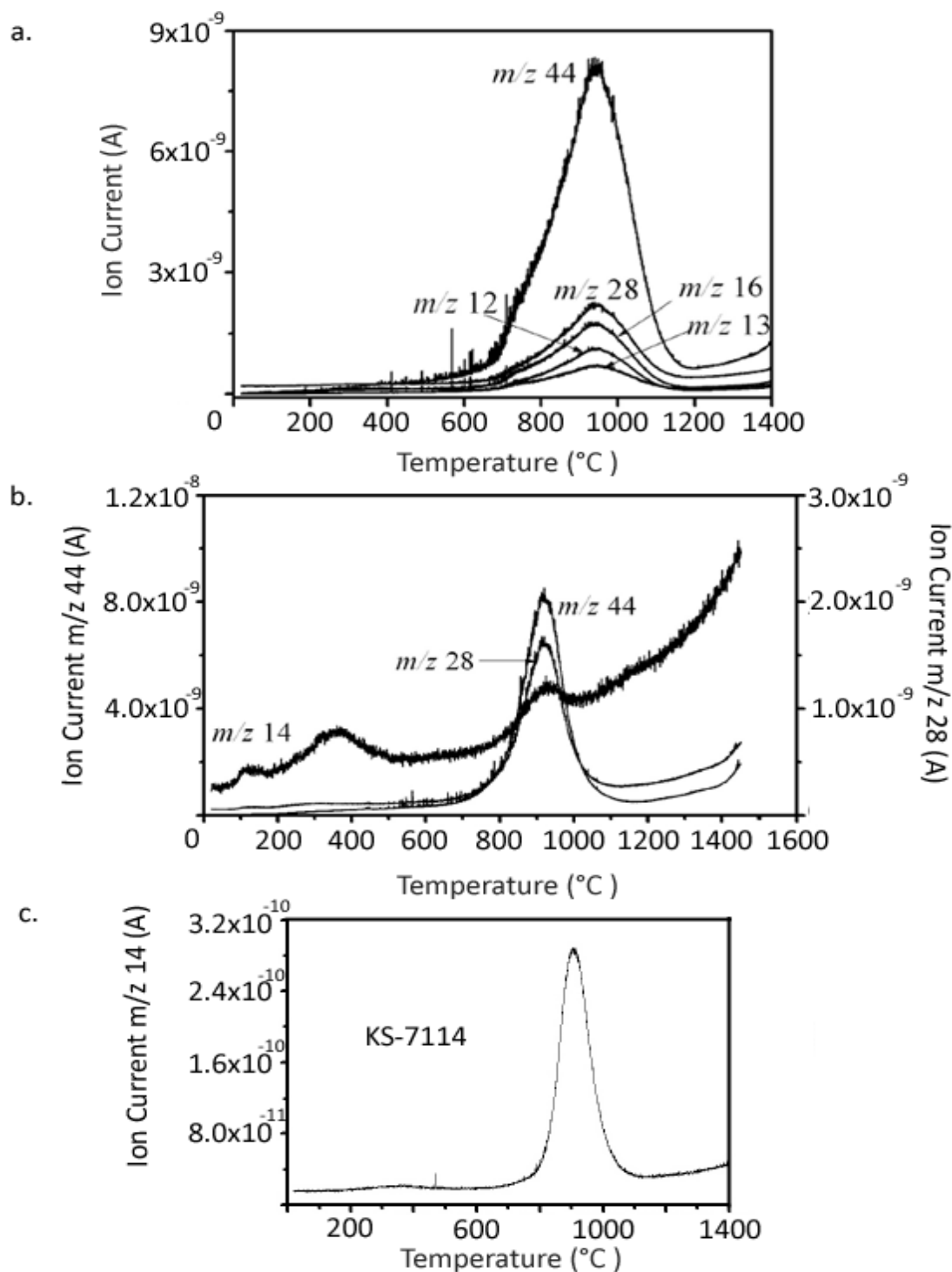


Fig. 1.3 Degassing profiles for (a) the m/z 44, 28, 16, 13 and 12 species. The degassing profile for m/z 13 is multiplied by a factor of 50 for plotting on this diagram. (b) m/z 14, 28, and 44 species. (c) m/z 14 (N^+) for cordierite sample 7114. From Geiger et al. (in press).

cordierites; more specifically it assumes excess m/z 28 peaks represent N_2 . Our results could serve as supplemental data to Geiger's experiments. Perhaps most importantly for our study, the work by Geiger et al. (in press) demonstrates that heating to temperatures of 1100°C should result in efficient extraction of N from the cordierites that were analyzed (see figure 1.3).

ANALYTICAL METHODS

Heating Experiments for Beryl

Heating experiments were undertaken to determine the N release characteristics for beryl and the optimal heating regiment for complete extraction of N for the isotopic measurements. To achieve this goal, one relatively inclusion-free beryl sample (collected in Pennsylvania) was cleaned with acetone and water, crushed, and sieved to produce four different grain-size separates: <0.125 mm, 0.125-0.25 mm, 0.25-0.50 mm, and 0.50-1.0 mm. Approximately 60 mg of sample were loaded into 6 mm o.d. quartz tubes with 1 g of CuO_x reagent and evacuated for 24 hours, with intermittent heating to approximately 100°C with a heat gun, on a vacuum manifold before sealing. Tubes were heated in a programmable furnace to either 1050 or 1100°C and for varying periods of time (180 to 300 minutes). Temperature and time variations were used to determine whether all the N is released from the mineral grains. Nitrogen concentrations and isotopic compositions were determined using the methods outlined below.

Nitrogen Analytical Methods

Beryl, cordierite, and mica N contents and isotopic compositions were analyzed using the carrier gas methods described by Bebout et al. (2007). Gem-quality beryl and cordierite (appendix a) were used in all experiments in order to reduce contamination

from mica inclusions potentially containing N in the form of NH_4^+ . Beryl and cordierite samples were crushed and sieved to reach a grain size of 0.25-1.0 mm and cleaned with purified water and an acetone solution (the latter used for quick drying). Grains were then examined under a microscope to ensure that they were relatively free of mica inclusions. Aliquots of cordierite and beryl (17-116 mg), or mica (10-40 mg), were loaded into quartz tubes with 1 g of CuO_x reagent and evacuated for 24 hours on a vacuum manifold before flame sealing. Tubes were heated at 1100°C for 180 minutes in a programmable furnace, and the cooling history was carefully regulated to ensure speciation of N as N_2 (see Bebout and Sadofsky, 2004, for description of methods). Extracted N (in the form of N_2) was purified in an all-metal extraction line, then transferred into a Finnigan MAT 252 mass spectrometer via a Finnigan Gas Bench II and a U-trap interface where small samples of N_2 were entrained into a He stream. Variations in the isotopic composition of N in unknown samples are defined in equation 1.2 where the standard (std) is atmospheric N_2 .

$$\delta^{15}\text{N} (\text{‰}) = \left[\frac{(\text{N}^{15}/\text{N}^{14})_{\text{sample}} - (\text{N}^{15}/\text{N}^{14})_{\text{std}}}{(\text{N}^{15}/\text{N}^{14})_{\text{std}}} \right] 10^3 \quad (1.2)$$

Carbon Analytical Methods

Carbon concentrations and isotopic compositions of cordierites were measured for 21 of the 30 samples, using dual-inlet mass spectrometry methods. The 21 samples that were chosen contained enough clean material to perform CO_2 analyses (i.e., to produce at least ~5 μmoles of CO_2 necessary for these analyses). Samples weighing 30-280 mg were loaded into quartz tubes with 1 g of CuO_x reagent and evacuated for 6 hours on a vacuum manifold before sealing with a gas torch. Tubes were then heated at 1050°C for

180 minutes in a programmable furnace, with the cooling history very carefully regulated to ensure speciation of C as CO₂. Temperatures used are comparable to those applied in other CO₂ studies in cordierites (Vry et al., 1990). The isotopic data are reported using standard notation for C relative to the VPDB (Vienna Pee Dee Belemnite) standard.

RESULTS

Testing of the Heating Regimen

Average measured N concentrations and isotopic compositions of the beryl separates from heating experiments, for the various heating temperatures and durations, show some scatter (figure 1.4), but also show an overall similarity at the larger grain sizes (0.25 to 1.0 mm diameter). Analyses of the <0.125 mm fraction produced $\delta^{15}\text{N}_{\text{air}}$ values of +7.7‰, higher than those of other size fractions (+5 to +6‰), and also higher concentrations. The elevated concentration and isotopic composition probably reflect contamination by mica inclusions, which are more abundant in the fine-grained split (based on microscopic observations). Contamination by mica would be expected to

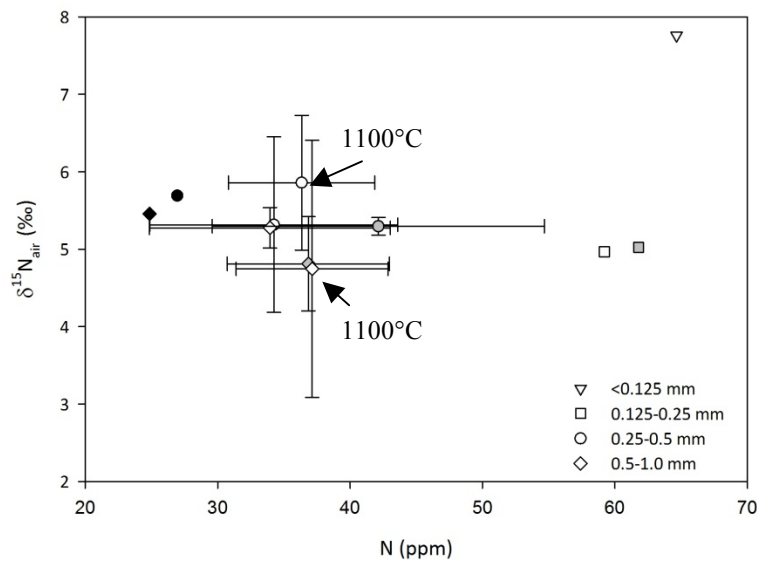


Fig. 1.4 Graph showing the effect of grain size, heating times, and heating temperatures on the release of nitrogen from the channels of a beryl sample. Points are averages from duplicate analyses and error bars indicate standard deviation. Variations in heating times are denoted by different colored symbols: 180 minutes – white, 240 minutes- gray, 300 minutes – black. All samples were heated to 1050°C unless otherwise noted.

produce a higher $\delta^{15}\text{N}$ value since, assuming equilibrium between NH_4^+ in the mica and N_2 in the beryl channels, NH_4^+ structurally bound in mica should be isotopically heavier than N_2 with which it is equilibrated (Hanschmann, 1981; Haendel et al., 1986). The next smaller size fraction, 0.125-0.25 mm, had somewhat higher concentrations of N, but the isotopic compositions fell within the ranges for the other grain sizes (excluding the <0.125 mm fraction).

A simple mass balance equation (equation 1.3) can be used to determine the extent of contamination from white mica in an analysis of a cyclosilicate phase (Mariotti et al., 1981, 1988). If δ is the isotopic composition and Q the mass of N_2 , then the mass and isotopic balance is:

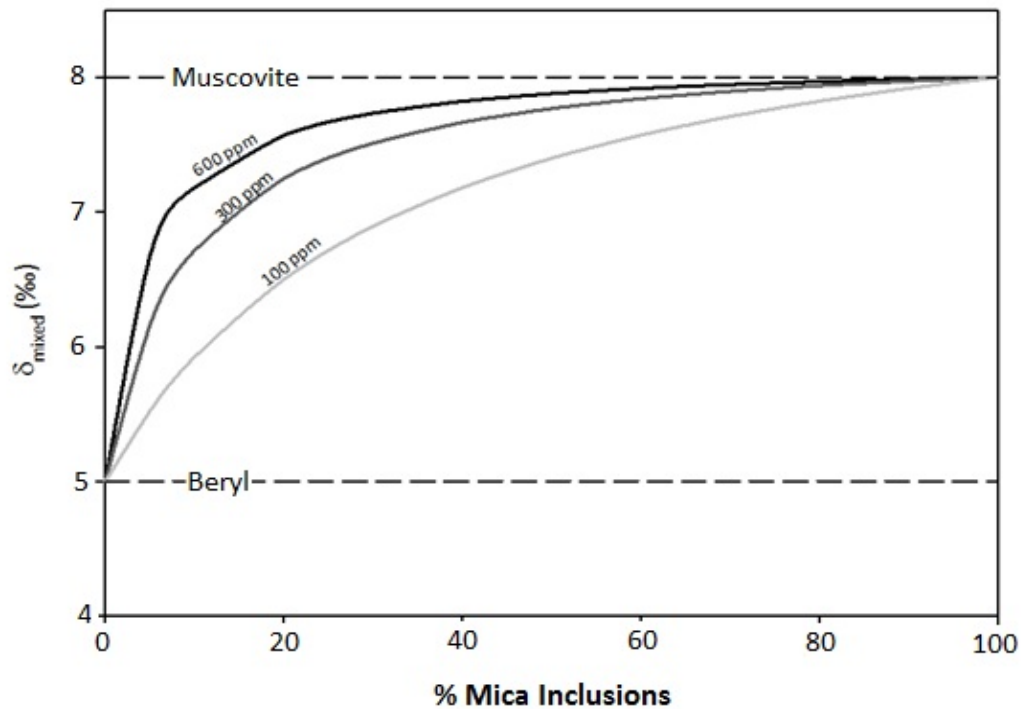


Fig. 1.5 Graph of Equation 1.1 illustrating the effect of mica inclusions and their concentrations on the overall isotopic composition of the host beryl. N concentrations of 25 ppm for beryl and 100, 300, and 600 ppm for mica were used and the equation assumes $\Delta^{15}\text{N} = 3\text{‰}$

$$\delta_{mixed} \cdot Q_{mixed} = (\delta_{mica} \cdot Q_{mica}) + (\delta_{beryl} \cdot Q_{beryl}) \quad (1.3)$$

Equation 1.3 applies to the simple mixing of two N-bearing minerals with different isotopic compositions (δ_{mica} and δ_{beryl}) to produce the final mixture (Q_{mixed}) with an intermediate isotopic composition depending on the relative contribution of N from each mineral (the latter dependent on the amount of mica present and its concentration). If this relationship is used to describe the beryl used in the heating experiment, the clean beryl would have a $\delta^{15}N_{air}$ of approximately +5‰ and the mica would be +8‰, assuming $\Delta^{15}N_{mica-beryl} = 3$ based on Hanschmann's (1981) calculations (at appropriate temperatures). Using typical N concentrations of beryl (25 ppm) and mica (100-600 ppm) for pegmatites, it is clear that only a few mg of mica can easily shift the isotopic composition by 1‰ (figure 1.5), again, assuming equilibrium conditions. In the case of the <0.125 mm fraction, a considerable amount of the very fine-grained material must have been mica to have shifted the isotopic composition to the degree that was observed. Examination of several grains from the coarser-grained splits by SEM showed that minor amounts of mica were indeed present, as fine-grained material attached to larger grains of beryl (figure 1.6a). These observations indicate that a careful examination of grains and the use of the 0.25-1.0 mm fraction will greatly reduce or eliminate mica inclusions and give a better estimate for the N_2 composition within the channels of cyclosilicates. After determining the effect of these mica inclusions on this test beryl sample, all cyclosilicate samples were examined under a microscope, before analyses, and only mica-free grains were hand-picked for the isotopic work. However, it is important to note that, particularly for metapelitic cordierite, which is commonly quite poikiloblastic, it is difficult to completely avoid inclusions of mica. The cordierite samples chosen for this study were

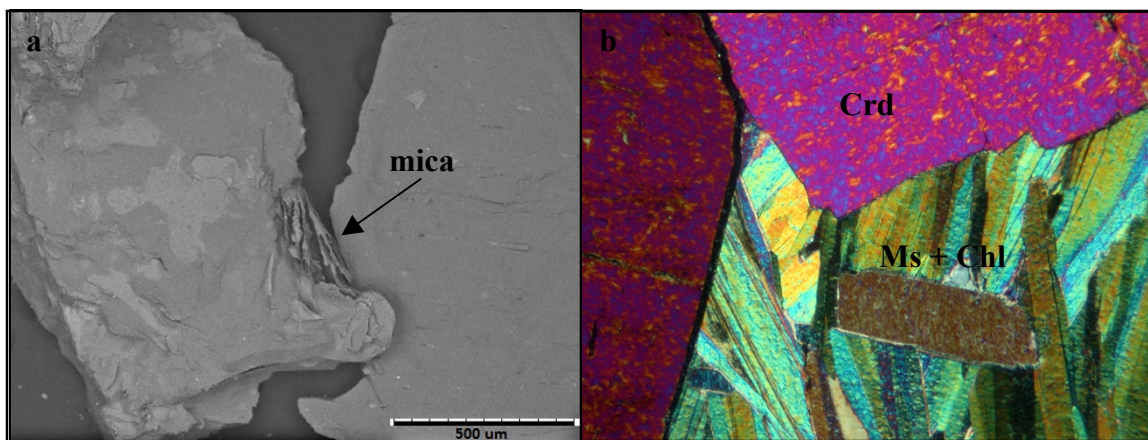


Fig. 1.6 (a) SEM image of the beryl grain size fraction 0.125-0.25 mm showing flakes of mica present. (b) Photomicrograph of iolite schist from Connecticut. Cordierite appears inclusion-free and is surrounded by a matrix of mica and chlorite.

largely the very clean samples on which Geiger et al. (in press) conducted their detailed degassing experiments. An additional uncertainty in this type of work is the relatively unlikely occurrence of fluid inclusions containing N species in abundances sufficient to impact the whole-mineral analyses.

As noted above, there was little variation between the N concentrations and isotopic compositions over the range of heating temperatures and times, but there was considerable scatter in the data likely due to the presence of small but varying amounts of mica as inclusions. According to diffusion theory, N release kinetics should be more profoundly affected by changes in extraction temperature than duration of heating. Based on this testing, heating at a temperature of 1100°C for 180 minutes was deemed adequate to remove all (or at least a very large proportion) of the N₂ from the samples. For micas, Sadofsky and Bebout, (2000) determined that this temperature is likely adequate for complete release of N from muscovite and biotite and, for cordierite, the step-heating degassing experiments of Geiger et al. (in press) demonstrate full release of channel volatiles by this temperature (see figure 1.3). A number of recent studies have concluded

that quantitative extraction of N is accomplished for a wide range of metasedimentary rocks, basalts and ultramafic rocks at the lower temperature of 1000°C (Bebout et al., 2007; Busigny et al., 2005; Halama et al., 2010; Li et al., 2007). Unlike in the step-heating experiments on Geiger et al. (in press), in which samples are heated at 10 °C/minute through a wide temperature range, our samples were heated to 1100°C at this same rate, but are were then held at this temperature for three hours before experiencing a very slow, controlled cooling sequence. Thus, there is every reason to believe that there would have been even more efficient N extraction from our samples than was demonstrated in the step-heating experiments.

Cordierite in Schist

Work on cordierite included analyses of several samples from chlorite-muscovite schists collected from Connecticut, USA. The photomicrograph of one of these samples in figure 1.6b demonstrates apparently inclusion-free cordierite crystals surrounded by muscovite and chlorite. For these rock samples, the mica-rich matrices contain up to 285 ppm N with $\delta^{15}\text{N} \sim +3.4\text{‰}$, whereas the cordierite grains contain no measurable N (i.e., with the heating experiments producing N_2 at blank levels). This contrasts with the results of the global survey presented in this thesis and the observation by Palya et al. (2011) that cordierites in granulite-facies metasedimentary migmatites at Mt. Stafford, Australia contain up to 350 ppm N with $\delta^{15}\text{N}$ similar to that of the whole-rocks.

Survey of Nitrogen in Cyclosilicates

Nitrogen concentrations and $\delta^{15}\text{N}$ values for each sample are presented in table 1.1. The beryls contain 11-39 ppm N_2 with $\delta^{15}\text{N}$ values ranging from +3.8 to +7.9‰. Beryl from a schist (80145) fell in the same range of isotopic compositions as beryls from

Table 1.1 Isotopic data for beryl and cordierite

	Sample	Beryl $\delta^{15}\text{N}_{\text{air}}$	Beryl N (ppm)	Musc. $\delta^{15}\text{N}_{\text{air}}$	Musc. N (ppm)	$\Delta^{15}\text{N}$ mica-beryl	Beryl $\delta^{15}\text{C}_{\text{VPDB}}$	Beryl C (ppm)
	80192	7.9	17	9.4	80	1.5		31
	23215	5.9	11	8.1	273	2.2	-8.5	48
	40597	4.0	25	8.3	305	4.3		
	1	3.8	18	6.7	41	2.9		28
	80145	5.1	39	8.7	632	3.6		
	Sample	Cordierite $\delta^{15}\text{N}_{\text{air}}$	Cordierite N (ppm)	Biotite $\delta^{15}\text{N}_{\text{air}}$	Biotite N (ppm)	$\Delta^{15}\text{N}$ mica-crd.	Cordierite $\delta^{15}\text{C}_{\text{VPDB}}$	Cordierite C (ppm)
Pegmatite/Partial Melts	88593	12.0	5	8.6	134	3.4		80
	80537	10.5	6	11	103	-0.5		31
	G-155a	5.1	17				-10.5	16
	C006	9.0	29				-6.9	936
	TUB-1	4.3	33				-13.6	195
	26230	7.5	38	1.8	70	5.7		
	C004	11.4	60				-8.8	600
	84264	7.4	67				-14.0	327
Mid-grade	Wards	16.9	8				-6.5	345
	25 Geco	10.4	19					
	WYO-2	5.1	30				-10.8	590
	118171	6.5	95				-8.4	694
Granulite Facies	X-1	4.7	41				-4.0	277
	42/IA	0.9	55				-12.0	543
	CL-177-1	30.0	71				-36.4	1200
	TA-5	7.0	101				-13.0	221
	129875	10.4	104					
	I3	4.8	162	7.8	116	-3.0		
	26539	9.9	232	0.5	65	9.3	-9.4	1099
	VS-1	5.9	273				-6.7	1039
	7114	2.9	634				-22.3	991
	S. India 1	3.1	923				-16.3	408
	89 V	3.6	1342					
	NE86A-24b	8.6	4525				-16.5	445
Uncategorized	CTSiM	9.0	27				-6.7	976
	10398	5.5	56	5.2	48	0.3		
	43090	8.3	89	2.7	86	5.5	-8.3	820
	33294	7.5	154	4.4	25	3.1	-9.3	614
	H06	2.0	446					
	106886	3.9	1457				-6.1	623

pegmatites, but contained more N₂, as shown in figure 1.7. Pegmatitic beryls have $\delta^{15}\text{N}$ values similar to those of organic matter in sediments (0 to +10‰; see Sweeney et al., 1978), perhaps indicating these pegmatites are derived from felsic intrusives representing partial melts of metasedimentary sources. Coexisting muscovite samples contain significantly more N (41-632 ppm) and have higher $\delta^{15}\text{N}$ values (+6.7 to +9.4‰) than the beryls. This pattern could potentially be explained by systematic partitioning of NH_4^+ into micas and N₂ into the channels of beryl (see discussion below). The direction and magnitude of this isotopic fractionation, $\Delta^{15}\text{N}_{\text{mica-beryl}} = +2.9\text{‰}$, is consistent with Hanschmann's (1981) calculated fractionation factors (see figure 1.7). Unfortunately, there is no record of the crystallization temperatures of the beryl samples, complicating efforts to determine whether there is a trend of increasing/decreasing $\delta^{15}\text{N}$ values or N concentrations with increasing temperature. However, some models suggest that pegmatites crystallize at or near the hydrous minimum melt temperatures of about 600°C (Jahns and Burnham, 1969), thus it is likely that this group of pegmatite beryls crystallized at similar temperatures with concentrations affected by other factors (e.g., the total N concentration of the “melt” from which the pegmatites crystallized, in turn potentially related to source regions and magmatic differentiation processes).

Coexisting biotites from pegmatites or melts contain more N (70-134 ppm) and typically have higher $\delta^{15}\text{N}$ values (+1.8 to +11‰) than their coexisting cordierites (figure 1.8). As the metamorphic grade increases to granulite facies, the biotites contain less N than the cordierites (65-116 ppm compared with 162-232 ppm). This corresponds to studies demonstrating that the N content of a rock decreases with prograde metamorphism, and in this case, it is reflected by the micas (Haendel et al., 1986; Bebout

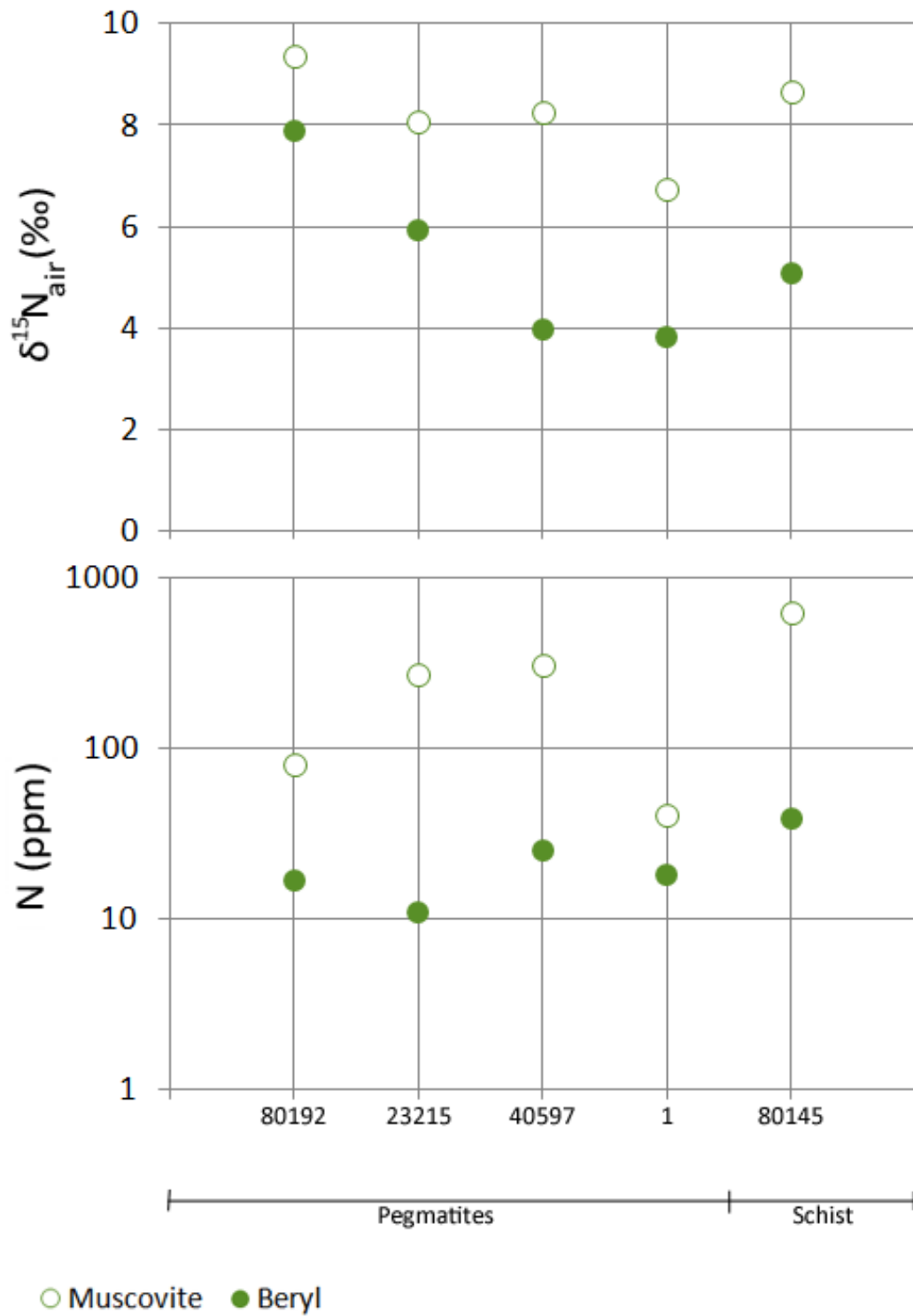


Fig. 1.7 Plot showing the ranges of $\delta^{15}\text{N}$ and N concentrations for beryl and coexisting muscovite. Muscovite always have higher concentrations of N and higher $\delta^{15}\text{N}$ than beryl.

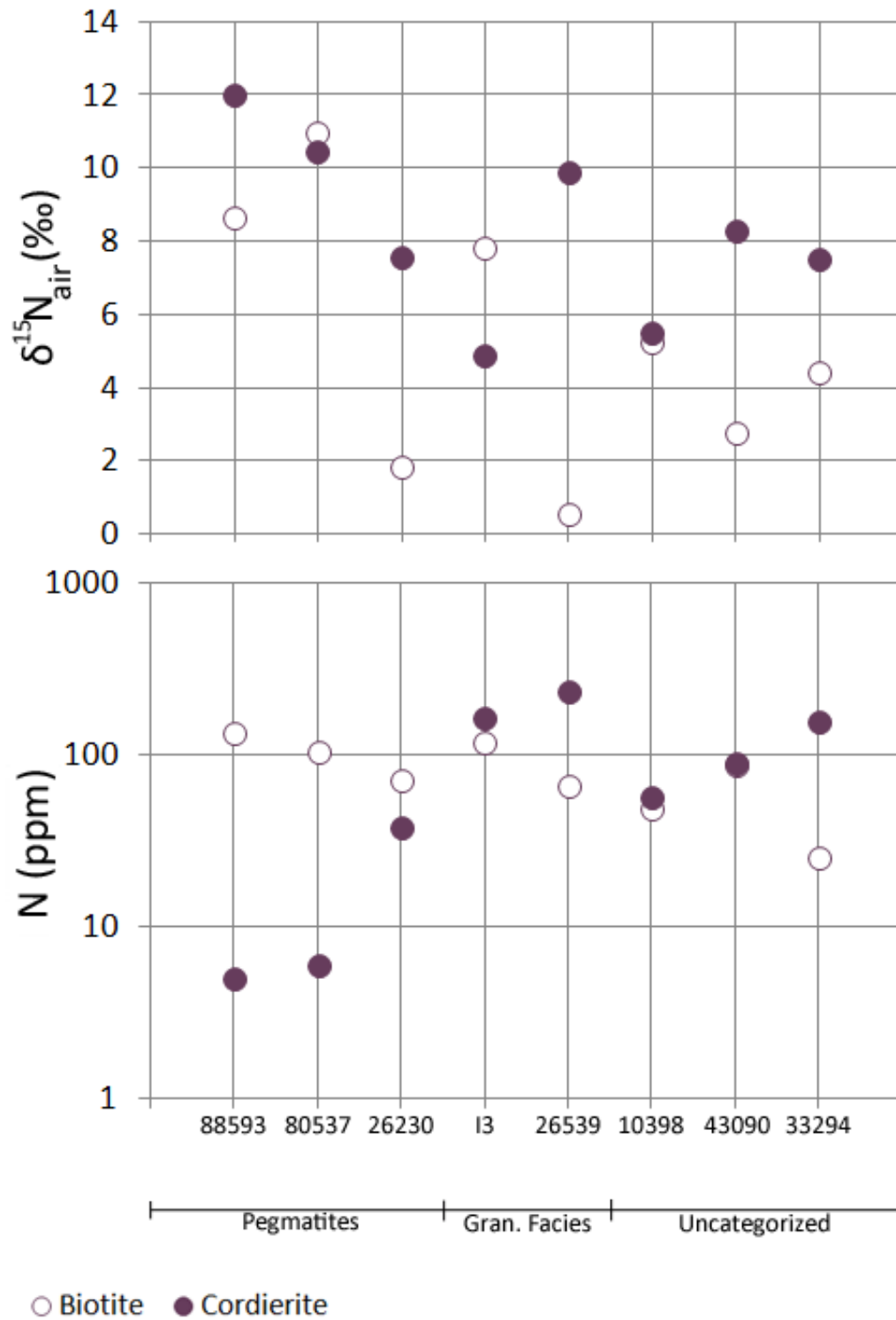


Fig. 1.8 Plot showing the ranges of $\delta^{15}\text{N}$ and N concentrations for cordierite and coexisting biotite. There is a scattered relationship between these pairs unlike beryl-muscovite pairs.

and Fogel, 1992; Jia, 2006). Unlike beryl and muscovite, the direction and magnitude of biotite-cordierite isotopic fractionation are not uniform (see comparison figure 1.7 vs. 1.8), suggesting a lack of simple relationship with temperature and that other factors must be considered. $\delta^{15}\text{N}$ for the cordierites investigated in this study ranges from +1 to +12‰, overlapping the range for organic N, with the exception of CL-177-1 (+30‰) and Wards (+16‰). The cordierites contain 5-4525 ppm of N_2 and show larger variations in $\delta^{15}\text{N}$ values and N concentration than the smaller set of beryl samples, but show a direct correlation between N concentration and metamorphic grade (table 1.1, figure 1.9). This pattern becomes clearer when temperature, rather than a broad category like metamorphic grade, is plotted vs. N concentration (see figures 1.10). The greater spread in isotopic compositions and concentrations in cordierite, compared with beryl, could be attributed to greater ranges in temperature, heterogeneity in sedimentary protoliths (see Sweeney et al., 1978), and differential effects of devolatilization (see Bebout and Fogel, 1992; Jia, 2006). It also appears that as N concentration increases in cordierites; $\delta^{15}\text{N}$ decreases with temperature (figure 1.11).

Survey of CO_2 in Cyclosilicates

Carbon concentrations and $\delta^{13}\text{C}$ values for each analyzed sample are presented in table 1.1. This work was undertaken to determine whether there are any obvious relationships between the concentration and isotopic compositions of channel CO_2 (C isotope compositions only) and channel N_2 (Vry et al., 1988). Beryls contain 28-48 ppm CO_2 with only one $\delta^{13}\text{C}$ value that was measurable (due to the low concentrations and need to analyze in dual-inlet mode) of -8.5‰. Cordierite samples are more variable in CO_2 concentration than the beryl samples, and show the highest concentrations in several

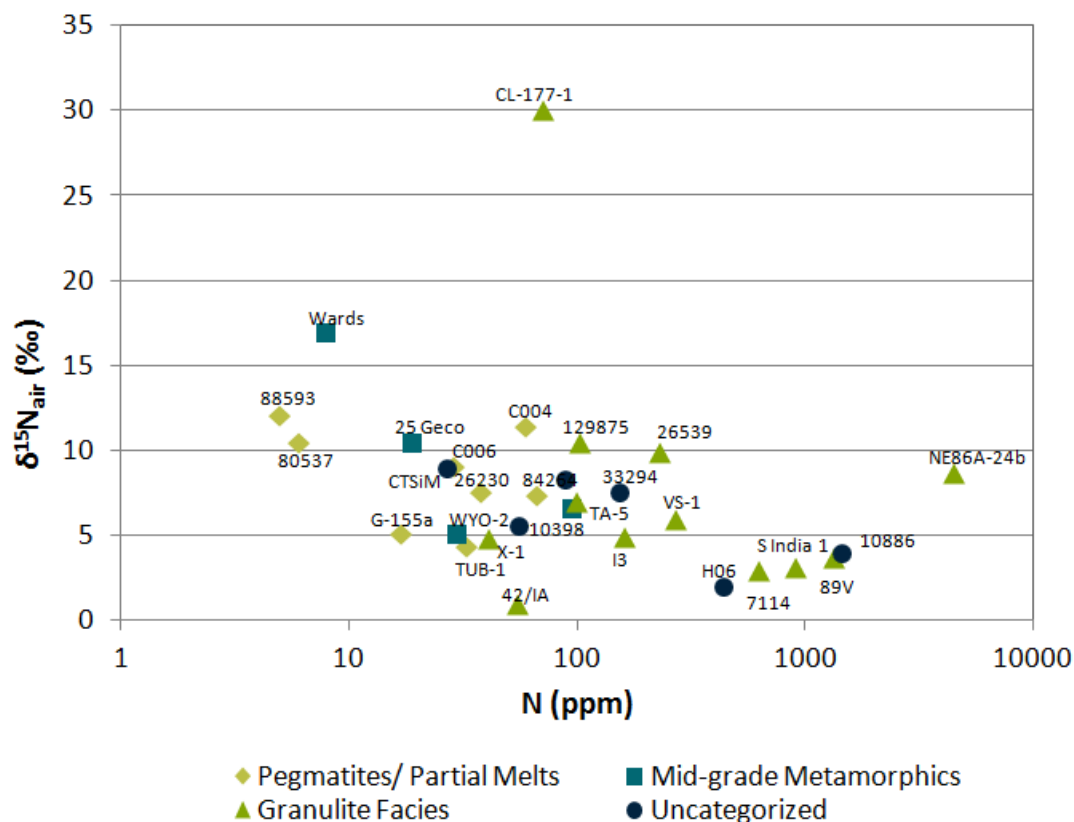


Fig. 1.9 Plot showing $\delta^{15}\text{N}$ vs. N concentration for all of the cordierites analyzed in this study. An increase in N concentration of cordierite correlates to lower $\delta^{15}\text{N}$ values.

of the higher-grade samples (see figure 1.15). The CO_2 data obtained in this study compare favorably with those obtained by Vry et al. (1990) in their C isotope study for the same samples, and by other analytical methods estimating the weight percent of CO_2 in cordierite (see appendix B; Vry et al., 1990; Bertoldi et al., 2004). $\delta^{13}\text{C}$ for cordierite samples ranges from -6 to -13‰, showing a similar range with that obtained by Vry et al. (1990). Sample CL-177-1 from the Pikwitonei granulite domain of Manitoba, Canada, had distinctive, very low $\delta^{13}\text{C}$ of -36.4‰ (very similar values were obtained for this sample by Vry et al., 1990). All but five samples analyzed for both N and CO_2 show higher concentrations of CO_2 than N within the channels, possibly demonstrating that

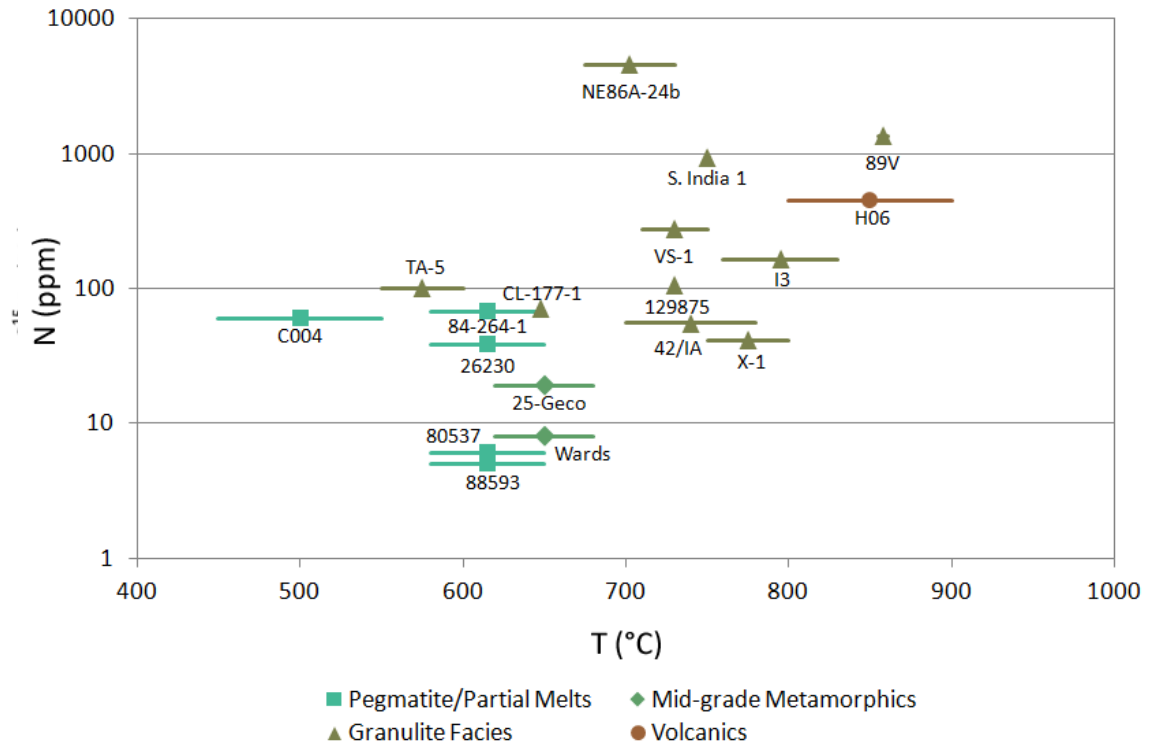


Fig. 1.10 Plot of N concentration vs. changing temperature of cordierite crystallization. There is a shift to higher concentrations when crystals are formed at higher temperatures.

CO₂ is typically more abundant than N₂.

DISCUSSION

Nitrogen Loss and Isotopic Fractionation During Metamorphic Devolatilization

Multiple studies have shown that the N concentration of a rock decreases and the $\delta^{15}\text{N}$ value increases with increasing metamorphism (Milovski and Volynets, 1966, 1970; Haendel et al., 1986; Bebout and Fogel, 1992; Bebout et al., 1999; Jia, 2006). This pattern can indicate a prograde devolatilization process intermediate in nature between batch volatilization and Rayleigh distillation, where N₂ is involved as the dominant species (see discussion by Bebout and Fogel, 1992). As metamorphic devolatilization progresses, the bulk rock continuously releases N depleted in ¹⁵N and the residual N in

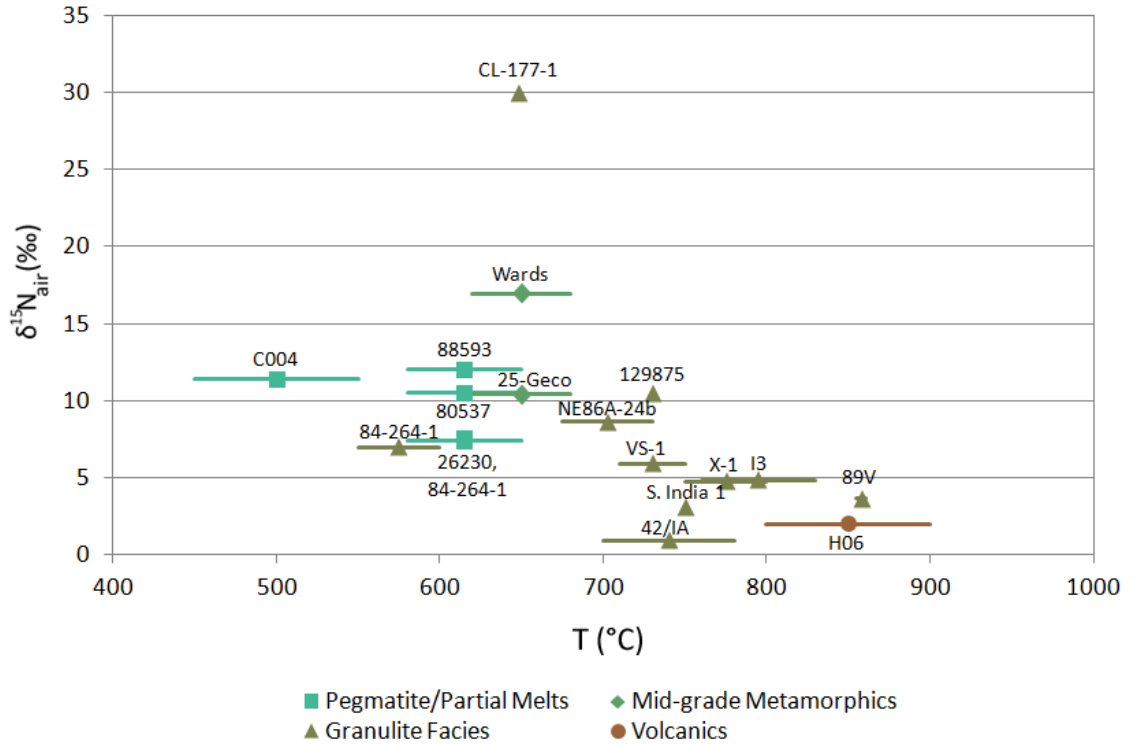


Fig. 1.11 Plot of $\delta^{15}\text{N}$ vs. changing temperature of cordierite crystallization. There is a shift to lower $\delta^{15}\text{N}$ values when crystals are formed at higher temperatures. This is the opposite trend of N concentration.

the rock becomes enriched in ^{15}N . Low-grade metamorphism (greenschist facies) typically mobilizes only 5-7% of a rock's total N, but this percentage increases considerably once the rock has undergone medium-grade, low- to medium-P/T metamorphism (epidote-amphibolite to lower amphibolite facies). Low- to medium-P/T, amphibolite- to granulite-facies metamorphism can result in loss of nearly 90% of the original sedimentary N (see Haendel et al., 1986; Jia, 2006). Interesting, relatively little N loss occurs in rocks along prograde metamorphic paths in the low-T, high-P/T conditions in forearcs of subduction zones (Busigny et al., 2003; Bebout et al., 2011).

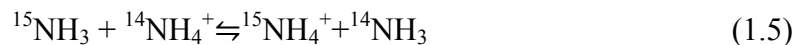
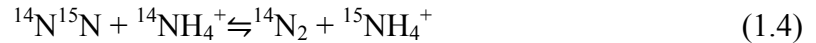
The opposite effect is observed for N_2 occluded in cordierites: an increase in N concentrations and decreased $\delta^{15}\text{N}$ values with increasing temperature (figures 1.10 and

1.11). One interpretation of this pattern could be as the host rock releases N during devolatilization, the cordierite incorporates it (or some part of it) and preserves it within its channels as the crystal cools (see similar conclusion made by Palya et al., 2010).

Therefore, the N₂ that becomes concentrated in cordierite with increasing metamorphic grade could be derived from the breakdown of micas and preferential release of ¹⁴NH₄⁺ (Lepezin et al., 1999). In previous studies, NH₄⁺ has been detected in the channels of cordierite and beryl (Mashkovtsev and Solntsev, 2002; Mashkovtsev and Thomas, 2005). Therefore, it is possible that the cordierites contain more than one species of N as temperatures increase, but that the relative proportions of these two species vary widely, from setting to setting, perhaps depending on oxygen fugacity imposed by the other minerals in the rock. This could serve as an explanation for the highly variable relationships among the N concentrations and isotopic compositions of coexisting cordierite and biotite (see figure 1.8).

Nitrogen Isotope Fractionation

The removal of N within the remaining rock during metamorphic devolatilization contributes to isotope fractionation between fluids and minerals (Haendel et al., 1986; Bebout and Fogel, 1992; Jia, 2006). The isotope fractionation factors for the following two reactions (equations 1.4 and 1.5) observed in this process were calculated by Scalan (1958) and Hanschmann (1981):



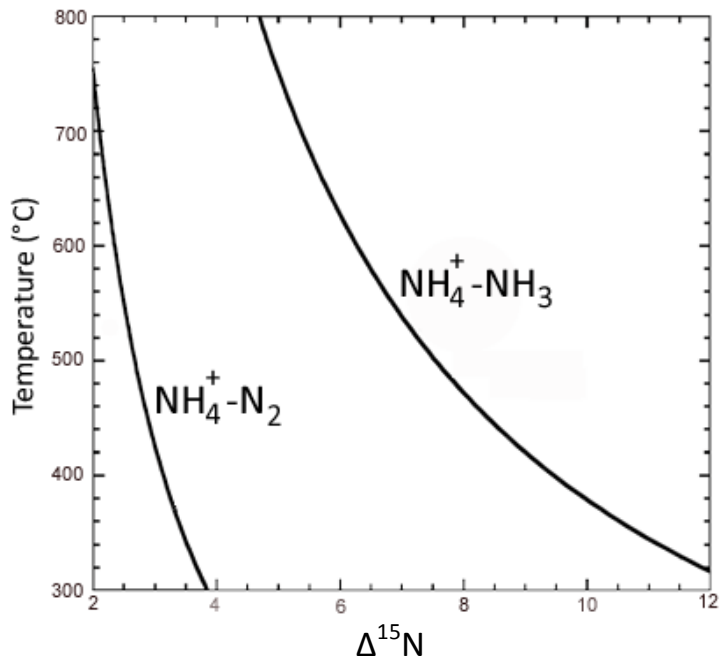
Although these fractionation factors are calculation-based, experimentally determined fractionation factors on step-heated phyllites show a similar temperature dependence relationship (Haendel et al., 1986).

These fractionation effects appear to be observed in the beryl-muscovite pairs (figure 1.7), and variations in the temperatures of equilibration could explain some of the scatter in the beryl-muscovite $\Delta^{15}\text{N}$. The direction and magnitude of this isotopic fractionation, $\Delta^{15}\text{N}_{\text{mica-beryl}} = 2.9\text{‰}$, is consistent with Hanschmann's (1981) calculated fractionation factors for equation 3, suggesting that N is stored in the channels of beryl as N_2 (figure 1.12). Unlike beryl and muscovite, the direction and magnitude of biotite-cordierite isotopic fractionation ($2.9 \pm 6\text{‰}$) are not uniform, overlapping the ranges of equations 1.3 and 1.4. As noted above, in these samples, N could be stored in channels as N_2 and NH_4^+ .

Nitrogen Behavior in the Context of Other Major and Trace Element Geochemistry

Pairing previously published electron-microprobe data (i.e., major element

Fig 1.12 Plot of spectroscopic results by Hanschmann (1981) showing estimated fluid-mineral N isotope fractionations. This work predicts that N_2 in fluids (within channels of cyclosilicates) would be isotopically lighter than structurally bound NH_4^+ with which it is equilibrated.



compositions) with the N data presented in this thesis provides new information regarding the effect of mineral chemical compositions on N behavior in cyclosilicates (See appendix B; Vry et al., 1990; Bertoldi et al., 2004). Removal of cations or H₂O in the channels of cyclosilicates appears to increase the potential for N storage. It was observed that as temperatures increased, H₂O weight percent in cordierites decreased corresponding with data reported in earlier studies (figure 1.13; Zimmermann, 1981; Vry et al., 1990; Lepezin et al., 1999). This decrease is vastly different from the increases in CO₂ and N₂ contents observed in cordierites with increasing temperatures. Ions such as Na⁺ or K⁺ may stay incorporated within the channels of cordierite, preventing occlusion of N. Pegmatite cordierites appear to contain more Na⁺ in general compared to pelitic rocks, but it is unclear whether this affects N occlusion (figure 1.15). There was no trend observed with K⁺ content, and a correlation of N and K concentrations might be expected if the N in the cordierites is largely as NH₄⁺ (due to the similar geochemical behavior of K⁺ and NH₄⁺). Some of the element trends may be solely temperature dependent, so determining if changes in N content are influenced by changes in major elements or just temperature may be difficult to isolate. It should also be noted that the studied cordierites likely occur in rocks with widely varying bulk compositions, complicating simple comparisons of cordierite mineral chemistry as functions of increasing P and T.

Nitrogen Variations

Differences in host rock bulk composition may add variances to the $\delta^{15}\text{N}$ of each cyclosilicate sample. Mica schists would have been derived from pelitic, high-N sediments, whereas gneisses or pegmatites would have formed from a quartz-rich melt probably deficient in N. Although my study did not explicitly consider host rock

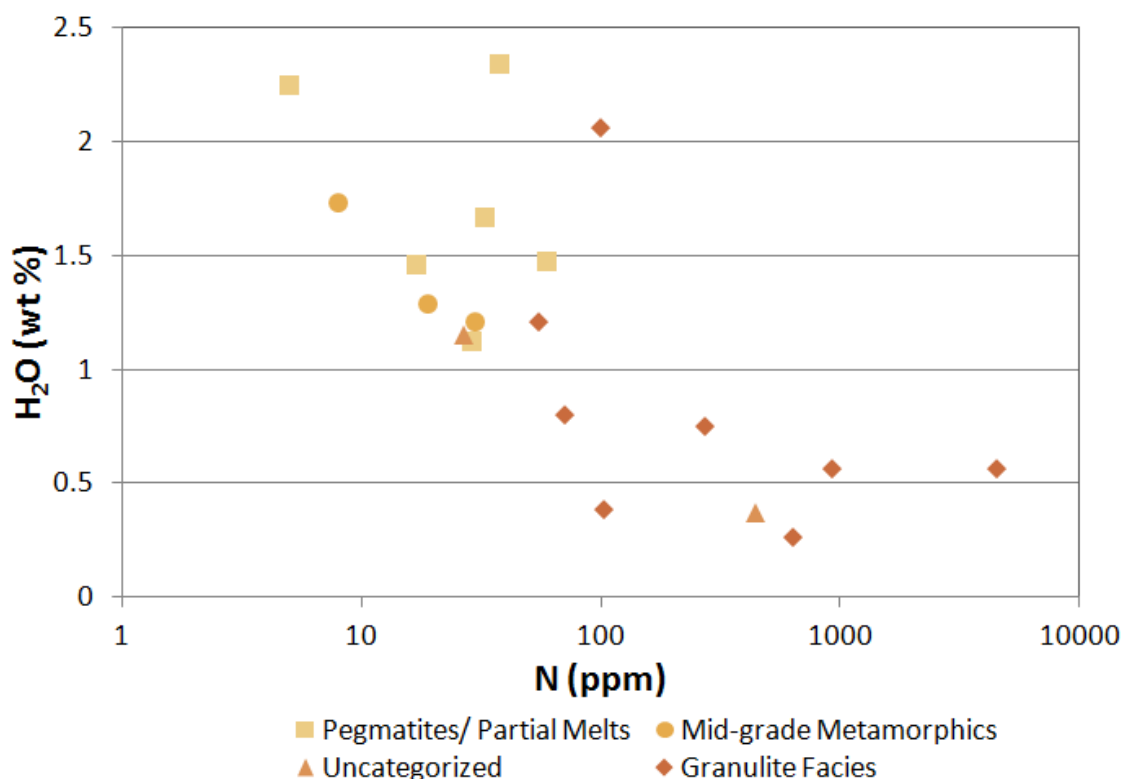


Fig. 1.13 Plot of weight % water against N concentration. The nitrogen content in cordierite channels increases as water content decreases. Water contents are from Vry et al. (1990) and Bertoldi et al. (2004).

composition, the bulk rock composition will influence the potential for what can be taken up by surrounding cyclosilicates. Later hydrothermal activity or alteration could shift the nitrogen values for cordierite depending on the composition of the altering fluid (probably the case for CL-177-1). Some of the samples also showed evidence of pinnitization, an alteration effect that incorporates chlorite, biotite, illite, or clay minerals into the cordierite (Fitzsimmons and Matthey, 1994). These minerals contain NH_4^+ and could shift the $\delta^{15}\text{N}$ values higher depending on the fractionation between N_2 and NH_4^+ at the alteration temperature. Similarly, metamorphism of organic matter could release NH_3 that undergoes an isotopic exchange with NH_4^+ ions bound to micas. If enough NH_3 is exchanged for NH_4^+ and their delta values differ significantly, then the $\delta^{15}\text{N}$ of the rock

could change (Haendel et al., 1986).

Future Work

It is still unclear how and when N is incorporated into the channels of cyclosilicates and further work needs to be undertaken in order to determine these mechanisms. Experimental studies paired with modeling could determine the maximum volatile contents of cyclosilicates coexisting with pure fluids (similar to work by Harley and Carrington, 2001). Closure temperatures of these minerals as well as N diffusion kinetics should be explored further to establish the extent of N release after peak metamorphism. Since gem-quality beryls and cordierites aren't commonly found in the field, microanalytical techniques need to be developed so smaller amounts of samples could be used and mica inclusions could be avoided. Although it is believed that N in the channels of cyclosilicates is primarily N_2 , spectroscopic techniques could be implemented to determine the relative proportions of N_2 and NH_4^+ . More detailed studies of N isotope behavior from multiple cyclosilicate samples from the same geologic setting might help to reduce variations attributable to site-specific factors, such as differing host bulk rock compositions. Once further data are collected and the mechanisms of N incorporation are better understood, N contents in channels could be used to establish the isotopic compositions and origins of the original metamorphic fluids.

CONCLUSION

This study serves as the first survey of N stored in the channels of cyclosilicates, likely as N_2 but, for some cordierites, possibly also as NH_4^+ . All of the analyzed samples of beryl and cordierite contained measurable quantities of N and had $\delta^{15}N$ values overlapping with those of organic N. For beryl samples, a lack of knowledge regarding

the temperatures of crystallization hampered consideration of the effect of temperature on the N compositions within channels. The beryl (and mica) obtained from a micaceous schist did show higher concentrations of N than beryls from pegmatites. That N in the beryl samples is in the form of N_2 is supported by the similarity in the $\Delta^{15}N_{\text{mica-beryl}}$ with the $\Delta^{15}N_{\text{NH}_4^+-N_2}$ fractionation factors calculated by Hanschmann (1981). It appears that, as cordierite experiences increasing temperatures, larger amounts of N are occluded into the mineral. This trend is the reverse of that seen within the surrounding rocks as they devolatilize N. The speciation of N in cordierites is probably a combination of N_2 and NH_4^+ , based on the non-uniform differences in $\delta^{15}N$ between the cordierite and surrounding biotite. It is possible that the N isotope system and cyclosilicates will be effective in studying volatile compositions at the highest temperatures the host rock experienced. However, a final decision on the degree of re-setting during protracted cooling awaits more careful study of closure temperatures for N_2 diffusion in cyclosilicate channels (and, for that matter, also for NH_4^+ in micas), perhaps with associated experimental study.

Chapter 2: Incorporation of Nitrogen into Melanophlogite, a Silica Clathrasil

ABSTRACT

The N isotope system can be used to investigate the interactions between low-temperature fluids and related minerals. Minerals that crystallize in low-temperature (<100°C) hydrothermal settings can potentially serve as long-term receptacles for volatiles, including organic components, if they remain robust during later thermal disturbances. This work focuses on the silica clathrasil melanophlogite, which houses guest molecules, including N₂, within its structural cages. Isotopic analyses can show trends in the compositions of fluids that interacted with such minerals during and after their formation, potentially providing information about sedimentary inputs.

Samples of melanophlogite investigated during this study came from a majority of the known occurrences (Italy and California, USA). Cages of melanophlogite are relatively enriched in N (132-1674 ppm), indicating that this phase can potentially trap and retain N. The $\delta^{15}\text{N}_{\text{air}}$ values for the N₂ in many of the analyzed samples (-6.1 to +5.7‰) show some overlap with values for organic N, but some of the melanophlogites have slightly negative isotopic values. Continued work on melanophlogite N incorporations should take into account the varying environments of crystallization of this phase and related N isotope fractionation in these environments.

INTRODUCTION

Study of the processes by which organic nitrogen (N) is incorporated and redistributed within the geosphere is essential to understanding modern volatile recycling and longer-term Earth degassing and atmosphere evolution (see Zhang and Zindler, 1993; Javoy, 1998). In order to fully exploit the N isotope system as a tracer of pathways of organic components into the solid inorganic Earth, numerous complex processes must be examined, including those involving low-temperature hydrothermal environments. Here, organic N can become incorporated into microporous phases that crystallize in low-temperature diagenetic and hydrothermal settings. In particular, silica clathrates are a group of interest because of their unusual physical properties, including their ability to enclathrate different molecules (Kolesov and Geiger, 2003). The silica clathrasil melanophlogite, being hydrophobic and thus unlike cordierite and beryl, does not contain the polar H₂O molecule, but contains instead significant amounts of CH₄, N₂, and CO₂ molecules that interact with the framework through weak van der Waals forces (Gies, 1983; Kolesov and Geiger, 2003). This study was aimed at investigating the guest N₂ in melanophlogite with reportedly up to 2 wt. % N₂ (Gies, 1983; Dunning and Cooper, 2002; Kolesov and Geiger, 2003; Navrotsky et al., 2003; Pouchard, 2006).

A careful study of N isotope compositions of N₂ “guest” molecules in melanophlogite has not been carried out, and a number of issues remain in determining whether or not melanophlogite can provide records of past organic activity. This preliminary study of melanophlogite will help determine the best analytical strategies for N isotope analyses of these low-temperature phases and provide an initial assessment of their potential utility in tracing the mobility of organic N. Toward these goals, a small

number of melanophlogites from around the world (provided by Dr. Charles Geiger of the University of Salzburg and by the American Museum of Natural History) were analyzed to determine the range of N concentrations and isotope compositions for this mineral.

BACKGROUND

Crystal Chemistry

Melanophlogite was first described by von Lasauix (1876) from Sicilian sulfur deposits, but it is now recognized in several additional localities in different low-T environments. Noted occurrences are in Italy (Skinner and Appleman, 1963; Grassellini Troysi and Orlandi, 1972), Bohemia (Žák, 1972), California (Cooper and Dunning, 1972), the Ukraine (Kropatsheva and Markov, 1975), and Oregon (Kohler et al., 1999). Although melanophlogite appears to be rare, it may be more common than we think and probably is often mistakenly identified as quartz or another low-temperature microcrystalline silica phase (e.g., chalcedony).

The silica clathrasil melanophlogite, $46\text{SiO}_2 \cdot 6\text{M}^{14} \cdot 2\text{M}^{12}$, has a microporous framework structure composed of corner-sharing SiO_4 tetrahedra that form two types of structural cages, the $[5^{12}]$ (represented in the formula by 6M^{14}) and $[5^{12}6^2]$ cages (6M^{14}) with the notation describing the polyhedra formed by the linkage between Si atoms (Figure 2.1). The mineral is considered a crystalline porosil where a host structure contains “guest” molecules within cages (Barrer, 1986). The $[5^{12}]$ cages are spherical (pentadodecahedral) with a free dimension of 5.7\AA and the $[5^{12}6^2]$ cages are ellipsoidal (tetrakaidecahedra) and have free dimensions of $5.8 \times 7.7\text{\AA}$; both are narrow enough to prevent diffusion of N_2 (Barrer, 1986; Xu et al., 2007). The different free dimensions of

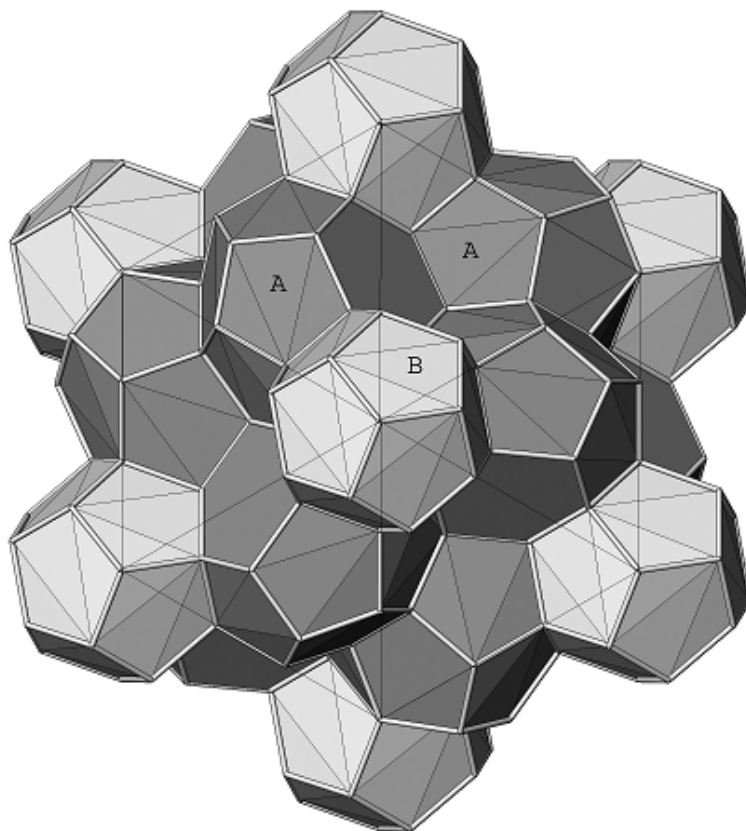


Fig. 2.1 A polyhedral representation of the crystal structure of melanophlogite (Gies, 1983; Hem et al., 2010) Polyhedral vertices are the Si atoms, white rods represent idealized Si-O-Si bonds. A represents $[5^{12}6^2]$ cages and B represents $[5^{12}]$ cages.

each cage determine what molecules can become incorporated.

Melanophlogite is tetragonal at room temperature, but undergoes a phase transition to a cubic shape at about 65°C (Gies, 1983). Under dry conditions, it can remain metastable at temperatures of up to 800°C, although it appears that the guest molecules are removed at the higher temperatures (Skinner and Appleman, 1963; Gies et al., 1982). In pure hydrothermal conditions, melanophlogite can be unstable between 300 and 500°C at 2 kbar, and in the absence of guest molecules it reverts to quartz. At much higher pressures (~8 kbar), melanophlogite will simply transform to coesite (Xu et al.,

2007).

Volatile Species

Both Appleman and Kamb (1965) were able to identify the presence of guest molecules in large polyhedral framework cavities. Kamb (1965) concluded that CO₂ and H₂O occurred in structural cages and thought that straight-chain hydrocarbons and sulfur could be present as well. A later study showed that CH₄, N₂, CO₂, and hydrocarbons were present in the cages of a melanophlogite crystal, however there was no evidence of sulfur molecules in either of the cages (Gies, 1982). It appears that melanophlogite always contains some amount of organic matter (Kortus, 2000). The molecules that are enclathrated into melanophlogite will depend on each cage: [5¹²] cages hold CH₄ while [5¹²6²] cages hold CO₂ and N₂ (Gies, 1993). CO₂ and CH₄ molecules align randomly in the cages and may be oriented this way as to optimize the interaction of these molecules with van der waals forces of the framework (Nakagawa et al., 2001). Guest molecules can even play a vital role in formation of melanophlogite by lowering the chemical potential of the lattice and forming cages (Nakagawa et al., 2001).

ANALYTICAL METHODS

Melanophlogite N contents and isotopic compositions were analyzed using the carrier gas methods described by Bebout et al. (2007). Extracted N (in the form of N₂) was purified in an all-metal extraction line, then transferred into a Finnigan MAT 252 mass spectrometer via a Finnigan Gas Bench II and a U-trap interface in which small samples of N₂ were entrained into a He stream. Between 9 and 17 mg of melanophlogite grains were loaded into quartz tubes with 1 g of CuO_x reagent and evacuated for 24 hours on a vacuum manifold before sealing. Tubes were heated at 1100°C for 180 minutes in a

programmable furnace, and the cooling history was very carefully regulated to ensure speciation of N as N₂ (see Bebout and Sadofsky, 2004, for description of methods). This temperature is adequate to release the trapped gas, because only 600°C is needed to create guest-free melanophlogite (Liu et al., 1997). Variations in the isotopic composition of N in unknown samples are defined in equation 1.2 where the standard (std) is atmospheric N₂.

RESULTS AND DISCUSSION

Nitrogen concentrations and $\delta^{15}\text{N}$ values for each sample are presented in table 2.1. The melanophlogites contained 132-1674 ppm N₂ with $\delta^{15}\text{N}_{\text{air}}$ values ranging from -6.1 to +5.7‰. Three of the five samples were enriched in ¹⁴N relative to air, and all but one of the samples fell within the isotopic range of organic N (sample 4361 is well within the $\delta^{15}\text{N}$ range of MORB).

Table 2.1 Isotopic and location data for melanophlogite

Sample	Location	$\delta^{15}\text{N}_{\text{air}}$	N (ppm)
40820	Italy	5.7	641
4361	Italy	-6.1	1674
4367	Italy	-2.8	132
81120	Italy	-1.5	154
Mt. Hamilton	Mt. Hamilton, CA	0.2	436

There are at least two possible models for the generation of the melanophlogite N₂ isotopic compositions: the melanophlogite could incorporate N₂ with exactly the isotopic composition of the N₂ in the fluid, or either ¹⁴N or ¹⁵N could be preferentially incorporated into the cages during the crystallization of the mineral. Negative $\delta^{15}\text{N}$ values could be interpreted as an enrichment of ¹⁴N, relative to a coexisting fluid with positive $\delta^{15}\text{N}$, within the cages of melanophlogite; however the isotopic composition of

the fluid is unknown making it impossible to evaluate this possible enrichment.

Relatively high concentrations in N suggest that N₂ is prevalent within the cages of melanophlogite and confirms initial studies on N₂ distribution in melanophlogite (Gies, 1983). For a melanophlogite sample from Mt. Hamilton, CA, Gies (1983) calculated a CO₂:N₂:CH₄ ratio of 1:3.6:1.8, where N₂ was the primary molecule. Variations in N₂ contents point to diverse fluid compositions, and this ratio could change depending on the environment of formation. According to Liu et al. (1997) temperatures of 1100°C are sufficient to remove all volatiles from the cages, suggesting that fractionation due to partial release of N₂ is not a significant factor.

Results for melanophlogite can be compared with N compositions for buddingtonite, an ammonium feldspar (NH₄AlSi₃O₈), which also forms in low-temperature hydrothermal settings. Previous studies reported $\delta^{15}\text{N}$ values of +7.7 to +10.6‰ for diagenetic buddingtonite in the Karoo Basin, South Africa (Svensen et al., 2008), and slightly negative $\delta^{15}\text{N}$ for buddingtonite from the Sulfur Bank Mine (near Clear Lake, California; see Bebout and Sadofsky, 2004).

Finally, recent speculation that the Mars surface contains abundant hydrated silica phases, perhaps including microporous silicates and clay minerals (Bish et al., 2003; Ruff, 2004; Bibring et al., 2006; Janchen et al., 2006), raises questions regarding the significance of some combination of these phases for surface/near-surface storage of H₂O, and potentially, organically-derived molecules such as CO₂, CH₄, and N₂. If present at the Martian surface, perhaps in part as alteration products of volcanic rocks and as cements in clastic rocks, N-bearing hydrous phases could serve in storing N₂. This may account for the missing N in recent Mars mass-balance models of Manicelli and

Banin (2003) based in part on the present-day N₂ content of the Martian atmosphere.

The research described above aimed at characterizing N₂ in melanophlogite is part of a preliminary study of the N₂ release, hosting, and retention characteristics during extractions from selected microporous silicates. Detailed assessment of the degrees of N retention in melanophlogite and other porous silicates, and how it is influenced by thermal history and the dimensions of any cages and channels, will be necessary in order to help identify the mineral phases that most effectively preserve records of the mobility and isotopic compositions of ancient organic N.

CONCLUSION

Melanophlogite is a useful mineral in determining how organic N is incorporated into microporous minerals in low-temperature hydrothermal settings. Cages of melanophlogite are relatively enriched in N (132-1674 ppm), indicating that this phase can be successful in trapping and retaining N. Nitrogen isotopic compositions of the N₂ in these cages (-6.1 to +5.7‰) show some overlap with organic N, but many of the samples have negative $\delta^{15}\text{N}$. The mechanisms of N₂ incorporation into this phase need to be explored further — one possibility is to evaluate whether these isotopic compositions directly reflect those of the fluid present during the crystallization of the melanophlogite.

Chapter 3: Transfer of Organically Derived Nitrogen into Mesozoic Volcanic Glasses

ABSTRACT

The N isotope system can be used to investigate the interactions between the biosphere and low-temperature minerals produced during hydrothermal alteration. Palagonized glasses can be altered chemically through alteration and the precipitation of organic NH_4^+ from pore fluids that in some cases have previously interacted with nearby sediments. Isotopic analyses of these glasses can show trends in alteration from pristine mantle to sedimentary/organic compositions.

This work focused on N stored in Mesozoic volcanic glasses from the Troodos ophiolite (Cyprus) and Stonyford complex (California, USA). Most of the palagonitized glasses in samples from both sites have higher N concentrations (up to 53 ppm) and $\delta^{15}\text{N}_{\text{air}}$ values (up to +7‰) than those of less-altered glass separates hand-picked from the same samples. All altered glasses have N concentrations higher than those of fresh MORB glass (typically less than 2 ppm N), reflecting significant N enrichment in these samples.

The observed shifts in N concentrations and $\delta^{15}\text{N}$ can be attributed to additions of sedimentary/organic N introduced by pore fluids. Circulation of hydrothermal fluids, perhaps in part induced by heat energy of nearby spreading-center magmatism, could have leached NH_4^+ from coexisting and overlying sediments that was then fixed into volcanic glasses. Glasses from both sites contain abundant textural evidence for microbial activity in the form of microtubules (ichnofossils). However, any role of this microbial activity in producing the N enrichments and elevated $\delta^{15}\text{N}$ values remains uncertain (and will be difficult to ascertain because of the very small volumes of microtubules in the

glasses). Enrichments of N (and the $\delta^{15}\text{N}$ of this N) in glasses from samples representing Earth's modern and ancient seafloor have direct relevance to considerations of modern global N subduction fluxes and ancient life, and similarly altered glasses on Mars and extraterrestrial bodies could serve as valuable life tracers.

INTRODUCTION

There are many reasons to examine the interactions between the biosphere and low-temperature minerals, including investigating the potential influence of these minerals (e.g., clays) as catalysts to biological activity (Banfield and Nealson, 1997; Ferris, 2005; Smith, 2005). Minerals that crystallize in either surface or diagenetic settings, and are robust to change during later thermal events, can serve as receptacles for organic components and can potentially preserve the signatures of past biological activity. Currently the study of the transfer of organic nitrogen (N) into the silicate Earth, and possible related isotopic fractionations related to this transfer, including the alteration of volcanic glasses has lagged behind the extensive studies of N isotopes in the biosphere, (Boyd, 2001; Holloway and Dahlgren, 2002). During alteration, these glasses are easily replaced by hydrous phases such as clays and zeolites and can experience microbial alteration (Staudigel et al., 2006).

Because metastable volcanic glass alters more readily than silicate minerals, the glass contributes more significantly to the overall chemical mass-balance of seafloor alteration (Staudigel and Hart, 1983). This glass alteration often occurs at extremely small scales and could have profound implications for geochemical studies in which glasses are preferentially analyzed to represent non-altered volcanic compositions (Cartigny et al., 2001). Previous work has demonstrated that altered oceanic crust on the seafloor can contain up to 18 ppm N with elevated $\delta^{15}\text{N}$ relative to that of unaltered oceanic crust (Busigny et al., 2005; Li et al., 2007). This N enrichment has been interpreted as reflecting interaction of these rocks with low-temperature hydrothermal fluids containing mobilized organic seawater N, thus stabilizing NH_4^+ -bearing alteration

minerals. Recently, it has been demonstrated that microbes colonize fractures in glassy basaltic rocks on the seafloor, extracting energy and nutrients from the glass by dissolving it, and leaving behind biomarkers. The role of this microbial alteration in the palagonitization that occurs in this environment remains uncertain.

Multiple complementary lines of evidence demonstrate that microbial life rapidly colonizes subaqueously-emplaced terrestrial glassy basaltic rocks (Torsvik et al., 1998; Banerjee and Muehlenbachs, 2003; Furnes et al., 2004; Banerjee et al., 2006; Benzerara et al., 2007; McLoughlin et al., 2009). Evidence for the microbial alteration of such rocks has been reported from modern ocean crust, ophiolites, and Archean greenstone belts extending to ~3.5 Ga. Surfaces of cavities etched by microbes often contain traces of microbial DNA or organic C residues and show uneven distributions on X-ray maps of biologically active elements such as N, K, P, and S (figure 3.1, 3.2). Altered glassy basaltic rocks have the potential to retain a variety of signatures of past biological activity, including microbial alteration textures (ichnofossils), element distributions, organic compounds, and distinctive isotopic compositions (Torsvik et al., 1998; Banerjee and Muehlenbachs, 2003; Furnes et al., 2004; Banerjee et al., 2006; Benzerara et al., 2007). The geological impact of glass bioalteration is substantial because it has been found everywhere in ocean drill holes, and it can play an important role in the glass alteration in any age crust, typically with optimum growth conditions between 15 and 80°C (Furnes and Staudigel, 1999; Walton and Schiffman, 2003). In addition, bioalteration was found in nearly all well-preserved ophiolites and greenstone belts suggesting that this process is pervasive to a significant depth, throughout geological time (Staudigel et al., 2008). Nitrogen incorporated into seafloor basalts by this process could

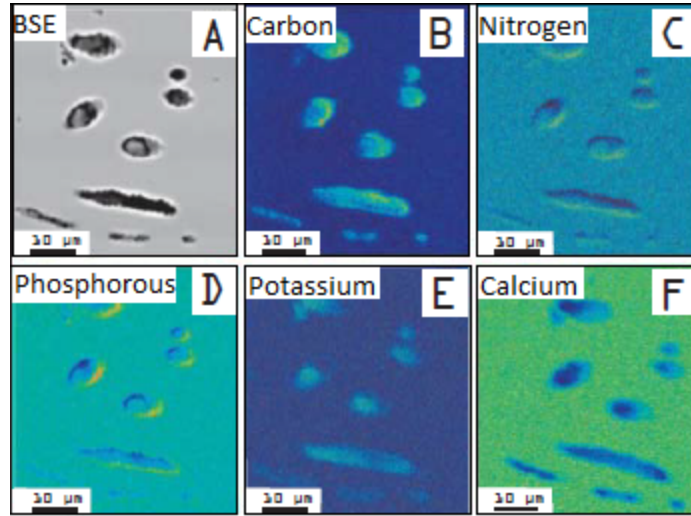


Fig. 3.1 Chemical element maps (EPMA-WDS), showing elevated levels of C, N, and P within tubular features. Low Ca levels indicate that C is not present as Ca-carbonate. K enrichment is likely due to the presence of palagonite-like alteration materials.

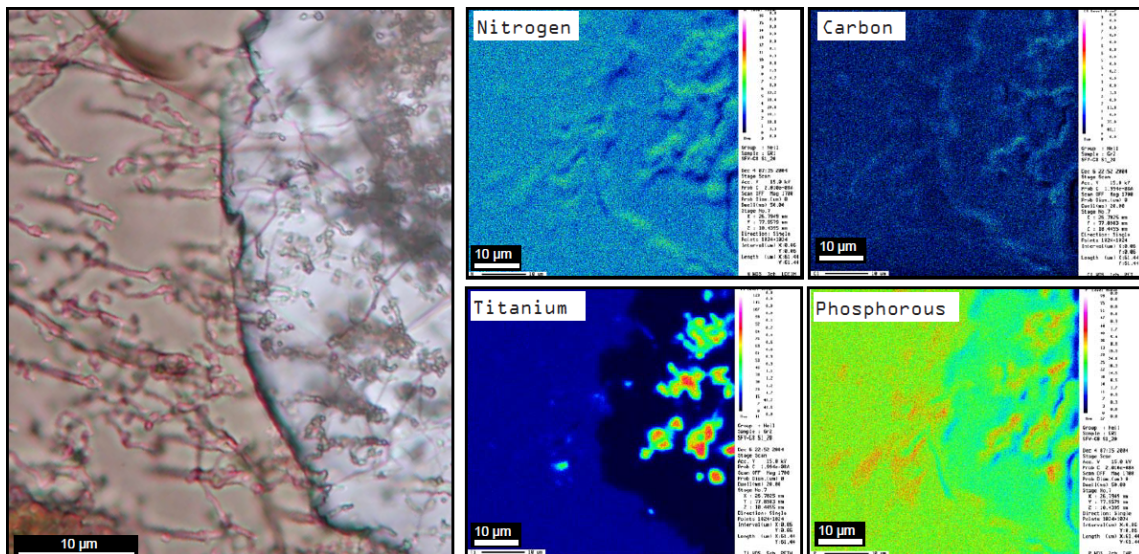


Fig. 3.2 Transmitted light photomicrograph and chemical element maps (EPMA-WDS), showing the transition between mineralized and mostly-hollow glass-hosted tubular textures from the Stonyford Volcanic Complex. Note the Tirich material in the mineralized zone, representing titanite-filled tubules. These samples demonstrate the transition between hollow features in fresh glass and titanite-mineralized features in ancient metabasalts.

contribute significantly to the N subduction budget (see Li et al., 2007).

Study of the extents to which silicate materials preserve N isotope records of organic-inorganic interactions in Earth's deep biosphere (and other extreme environments) over long periods of geologic time could have implications for the exploration for signs of extraterrestrial organic activity. On Mars, it is possible that hydrous phases are responsible for some storage of N (in addition to H₂O), and spectral data for the Mars surface have been interpreted as indicating the presence of hydrous phases such as clays and zeolites in surface/near-surface Mars (Bish et al., 2003; Manicelli and Banin, 2003; Ruff, 2004; Newsom, 2005; Poulet et al., 2005; Janchen et al., 2006; Wyatt and McSween, 2006). There has been speculation that zeolites and clays could occur on Mars both as alteration products after volcanic glass and as cement in sandstones (Basu et al., 1998; Towell and Basu, 1999; Chan et al., 2005).

This study presents analytical results for N content and $\delta^{15}\text{N}$ on palagonitized glasses from the Troodos Ophiolite and Stonyford volcanics (both Mesozoic) as a means to assess the potential of these materials as biological tracers. Previous studies have analyzed whole-rock samples from Archaen basalts (Abitibi Complex, Quebec, Canada) and the modern seafloor using methods similar to those described below (Busigny et al., 2005; Li et al., 2007; Andersen et al., 2010). For ODP Site 1256 (offshore of Costa Rica), data for altered glasses were compared with those for relatively pristine glasses from the same locality to determine the extent to which the alteration and related N enrichment is controlled by the abundance and N concentrations of the variably altered glasses (Li et al., 2007). Microbial ichnofossils have been described for both the Troodos and Stonyford suites (see the photomicrographs in figure 3.3), and Andersen et al. (2010)

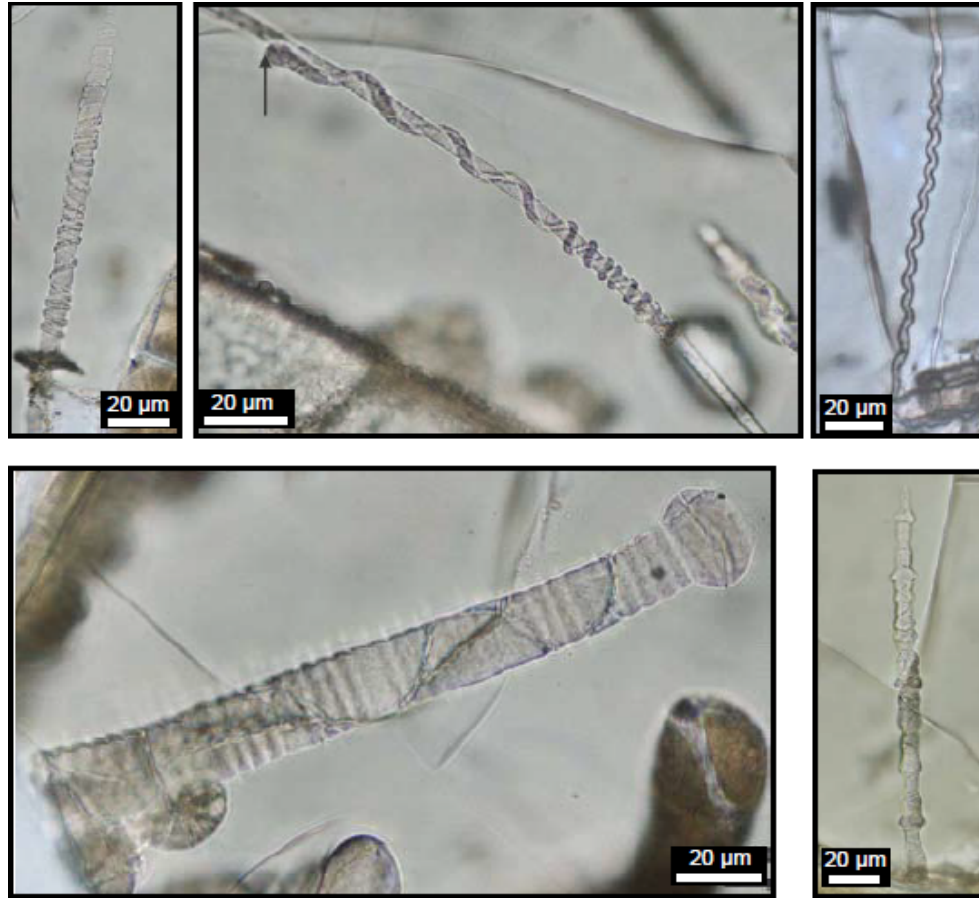


Fig. 3.3 Examples of tubular bioalteration textures from the Troodos ophiolite, Cyprus; including spiral-and-tube, spiral, and segmented morphologies. These are extremely suggestive of a biological origin.

identified similar textural features in the greenschist-facies, 2.7 billion-year-old Abitibi pillow basalts.

BACKGROUND

Troodos Ophiolite

The Cretaceous Troodos ophiolite of Cyprus contains all the components of a complete ophiolite as well as an abundance of fresh glass and has been investigated extensively (e.g. Panayiotou, 1980; Robinson et al., 1983; Malapas et al., 1990). Over half of the volcanic rocks are pillow lavas, and the remainder are breccias associated with

pillows and sheet flows (Schmincke and Bednarz, 1990). Textural studies have revealed that the altered basaltic glasses reach to depths of at least 550 m into the volcanic basement (Thorseth et al., 1995; Furnes et al., 1996, 1999; Fisk et al., 1998; Torsvik et al., 1998; Fisk, 1999; Furnes and Staudigel, 1999).

Stonyford Volcanics

The Stonyford volcanic complex is a thick accumulation of pillow basalt and diabase of Late Jurassic age in the northern Coast Ranges of California (Brown, 1964; Hopson et al., 1981; Shervais and Kimbrough, 1987). Glasses in this area were first reported by Brown (1964) and occurs within the pillow basalts. Lava flows in the Stonyford volcanics include both pillow lava and sheet flows, but massive sheet flows seem to be the dominant flow type. The base of the seamount sequence, which lies to the SW and west, is dominated by massive tholeiitic flows, with intercalations of pillow lava (Shervais et al., 2005).

ANALYTICAL METHODS

Nitrogen contents and isotopic compositions of volcanic glass were determined using the carrier gas methods described by Bebout et al. (2007). Under a binocular microscope, glass samples were separated into clean (black and glassy) and altered (glass with dull brown encrustations) fractions and then crushed. About 100-500 mg of clean and altered glass samples were loaded into quartz tubes with 1 g of CuO_x reagent and evacuated for 24 hours on a vacuum manifold before sealing. Tubes were heated at 1050°C for 180 minutes in a programmable furnace, and the cooling history was very carefully regulated to ensure speciation of N as N₂ (see Bebout and Sadofsky, 2004, for description of methods). Nitrogen extracted (in the form of N₂) was purified in an all-

metal extraction line, then transferred into a Finnigan MAT 252 mass spectrometer via a Finnigan Gas Bench II and a U-trap interface where small samples of N₂ were entrained in a He stream. Variations in the isotopic composition of N in unknown samples are reported using the conventional delta notation in equation 1.2 where the standard is atmospheric N₂.

RESULTS

Nitrogen concentrations and $\delta^{15}\text{N}$ values for each sample are presented in table 3.1 and figure 3.4. Glasses from Troodos contain 2-14 ppm N for cleaner glasses and 5-53 ppm for the more altered glasses. The $\delta^{15}\text{N}_{\text{air}}$ of those glasses range from -7.3 to +5.5‰ for clean glasses and -5.3 to +7.0‰ for altered glasses. Glasses from Stonyford contain 3-33 ppm N for clean glasses and 13-45 ppm for altered glasses. The $\delta^{15}\text{N}$ values of those glasses range from -7.2 to -3.9‰ for clean glasses and -6.3 to -2.6‰ for altered glasses.

Table 3.1 Isotopic data for volcanic glasses

Sample	Clean		Altered	
	$\delta^{15}\text{N}_{\text{air}}$	N (ppm)	$\delta^{15}\text{N}_{\text{air}}$	N (ppm)
CYP-01	-1.8	2	1.8	6
CYP-02	-7.3	2	-5.3	5
CYP-03	4.3	12	6.1	53
CYP-04	5.5	14	7.0	49
CYP-05	4.5	9	1.4	9
CYP-009	-3.8	10	-1.5	8
CYP-011	0.4	6	-2.5	7
SFV-G2	-7.2	22	-2.6	30
SFV-G3	-5.4	33	-3.0	45
SFV-G4	-6.7	19	-6.3	28
SFV-G5	-3.9	18	-4.3	13
SFV-G8	-4.7	3	-5.7	16

The more palagonitized glasses from the Troodos ophiolite and Stonyford volcanic typically have higher N concentrations (up to 53 ppm) and $\delta^{15}\text{N}$ values than less-altered glass separates. Some Stonyford glasses (with and without alteration) are enriched in N relative to fresh MORB glass, but have mantle-like $\delta^{15}\text{N}$ of -8 to -4‰. $\Delta^{15}\text{N}_{\text{altered-unaltered}}$ for Troodos samples ranged from -3.1 to +3.7‰ and -1.0 to +4.6‰ for Stonyford samples, presumably representing a range in the degrees of alteration.

DISCUSSION

Nitrogen Enrichment in the Glasses

All of the altered glass samples analyzed in this study (figure 3.4) have N concentrations higher than those of “fresh” MORB (the latter typically containing less than 2 ppm N; see Cartigny et al., 2001), reflecting significant N enrichment in these samples relative to their unaltered counterparts. For the Stonyford glasses, the observed shifts from MORB N concentrations, could indicate that early-formed palagonite incorporated mantle-derived N, and later-formed palagonite incorporated sedimentary/organic N introduced by pore fluids. Circulation of hydrothermal fluids induced by the magmatic activity could have leached NH_4^+ from coexisting and overlying sediments. This NH_4^+ could then have been fixed into secondary clay minerals and bound to the glasses.

Since both sample suites are of the Mesozoic age, the variation between the Troodos and Stonyford samples cannot be simply explained by time-dependent intensities of incorporation of secondary N as the sediment cover progressively thickens. This is observed as both sets of samples have N concentrations that overlap one another. The difference in starting (unaltered) glass samples, however, can explain the variations in

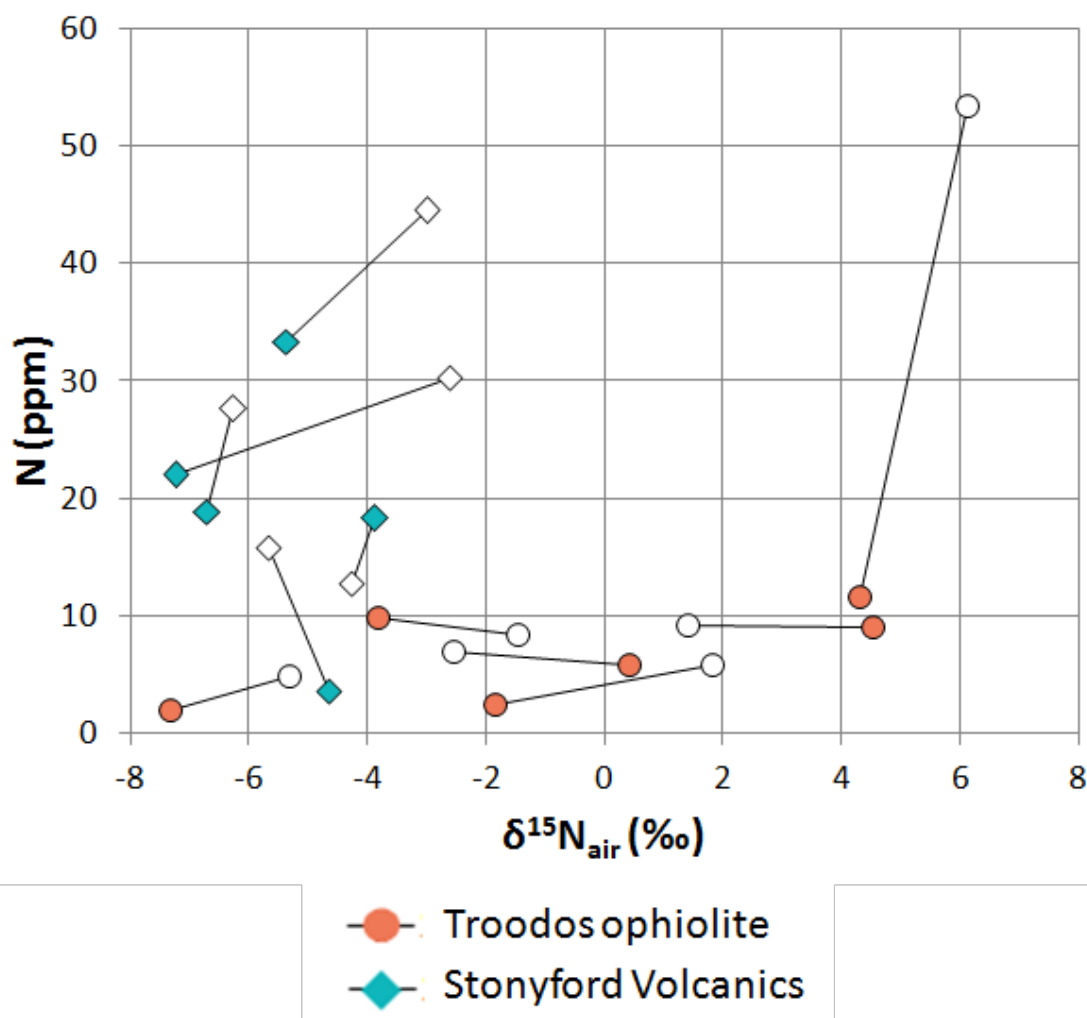


Fig. 3.4 Plot of N concentration and $\delta^{15}\text{N}$ for Stonyford and Troodos ophiolite glasses. Shaded shaes represent clean, unaltered glasses and unfilled shapes represent palagonized samples. Corresponding samples are connected with a tie-line.

palagonized glass isotopic values. Higher starting $\delta^{15}\text{N}$ values will subsequently lead to higher $\delta^{15}\text{N}$ values after alteration. Higher values could be attributed to differences in source magmas and hydrothermal activity.

Importance for Subduction Zone N Cycling Budgets

The geochemistry of N discharged by magmatism at mid-ocean ridges and in volcanic arcs has been investigated in some detail, including work focused on several

convergent margins that greatly improves our understanding of N return in arcs (e.g., Fischer et al., 2002, 2005; Hilton et al., 2002; Snyder et al., 2003; Zimmer et al., 2004; Li et al., 2007). Altered oceanic crust, including altered glasses, subducting into modern trenches could play a key role in the crust-mantle cycling of N (Li and Bebout, 2005; Li et al., 2007). Li and Bebout (2005) highlight that, because the volume of oceanic crust is far greater than that of the overlying sediments, the N subduction budget in oceanic crust could be comparable to that in sediments and must be considered in any attempt to mass-balance input and output N fluxes across subduction zones (Bebout, 1995; Hilton et al., 2002).

CONCLUSION

This study serves as an exploratory study of the incorporation of N, through low-temperature hydrothermal alteration, into Mesozoic volcanic glasses from Cyprus and the Franciscan complex. All samples investigated in this study contain measureable quantities of N, and palagonitized glasses from both sites typically have higher N concentrations (up to 53 ppm) and $\delta^{15}\text{N}$ values than less-altered glass separates from the same samples. All altered glasses have N concentrations higher than those of fresh MORB (typically less than 2 ppm N), reflecting significant N enrichment in these glass samples relative to the concentrations that can be attributed to magmatic processes. The observed shifts in N concentrations and $\delta^{15}\text{N}$ can be attributed to incorporation of sedimentary/organic N introduced by pore fluids. Circulation of hydrothermal fluids, perhaps induced by heat from the nearby magmatism, could have leached NH_4^+ from coexisting and overlying sediments and then fixed it into glasses. Alternatively, this alteration could continue during the longer-term transit of oceanic crust across ocean

basins and toward subduction zones at which it will contribute N to the budget of N subducting into the mantle. These findings also may be relevant to planning strategies in the search for modern and ancient life on Mars and other extraterrestrial bodies.

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Appendix A Cyclosilicate Sample Information			
Sample	Mineral	Locality	Rock type and/or facies and/or mineral assemblage and/or P–T estimates [Donor]
80192	Beryl	Buckfield, Maine	Var. morganite; Pegmatite; Brl-ms-kfs-qtz [AMNH]
23215	Beryl		Var. morganite; Pegmatite; Brl-ms [AMNH]
40597	Beryl	Minas Gerais, Brazil	Var. emerald; Pegmatite; Brl-ms [AMNH]
1	Beryl	Kunar, Afghanistan	Var. aquamarine; Pegmatite; Brl-ms [KL]
80145	Beryl	Salzburg, Austria	Var. emerald; Schist; Brl-ms [AMNH]
WYO-2	Cordierite	Laramie Range, Albany Co., WY, USA	Metasomatic deposit in a metanorite; Crd (1, 2, 3, 4, 5); [CG]
CL-177-1	Cordierite	Pikwitonei Granulite Domain, MB, Canada	Granulite; Qtz(rt)-plag-kfs-bt-crd-grt-ilm-po-py-sp-zrn; 6.1–6.8 Kb, 648°C (1, 6); [CG]
Wards	Cordierite	Manitouwadge, ON, Canada	Upper amphibolite; Ged-col-bt-plag-qtz; 6±1 Kb, 650±30°C (1, 7); [CG]
25 Geco Mine	Cordierite	Geco Mine, Manitouwadge, ON, Canada	Amphibolite; Crd-po-ccp-py-qtz-bt-fsp; 6±1 Kb, 650±30°C (1, 7, 8, 9); [CG]
NE86A-24b	Cordierite	Sturbridge, MA, USA	Granulite (probably lower temp, in pocket); Qtz-plag-kfs-bt-crd-grt-ged-sill-rt-zrn-opaques; 6.3 Kb, 675–730°C (1, 10); [CG]
118171	Cordierite	Richmond, NH, USA	Crystals in a quartz matrix from a mica schist; Crd-qtz-tur-rt-(ky)-crn-st-ath (1, 11); [CG]
80537	Cordierite	Haddam, CT, USA	Crystals in pegmatite “dike” in bt-gneiss; Bt; 580–650°C (4, 8, 12, 13, 14, 15, 16, 17); [AMNH]
88593	Cordierite	Haddam, CT, USA	Crystals in pegmatite “dike” in bt-gneiss; Crd-qtz-mic-ab-tur-grt-zrn-col-bt-cbri; 580–650°C (4, 8, 12, 13, 14, 15, 16, 17); [CG]

Appendix A	Continued	
26230	Cordierite Haddam, CT, USA	Crystals in pegmatite “dike” in bt-gneiss; Crd-qtz-mic-ab-tur-grt-zrn-col-bt-cbtl; 580-650°C (4, 8, 12, 13, 14, 15, 16, 17); [AMNH]
84-264-1	Cordierite Guilford, CT, USA	Pegmatite vein cutting Schist; Crd-qtz-feld-bt-gneiss (1, 4); [CG]
H06	Cordierite El Hoyazo Volcano, SE Spain	Crd xenocryst found as loose material from weathered lava; 5-7 Kb, 850±50°C (18, 19, 20); [CG]
VS-1	Cordierite Chiaravalle, Calabria, Italy	Granulite facies; Grt-crd-sill-bt-plag-qtz; 5-6 Kb, 730±20°C (21); [CG]
10398	Cordierite Bavaria, Germany	Bt [AMNH]
TUB-1	Cordierite Dolní Bory, Czech Republic	Pegmatite; Kfs-ab-qtz-tur-ms-ap-grt (8, 22, 23, 24, 25); [CG]
43090	Cordierite Telemark, Norway	Bt [AMNH]
33294	Cordierite Telemark, Norway	Bt [AMNH]
106886	Cordierite Telemark, Norway	Bjordammen Pegmatite (14); [CG]
C004	Cordierite Søndeled, Norway	Quartz pegmatite; Qtz-crd (pinnitized); 3-4 Kb, 500±50°C (13); [CG]
7114	Cordierite Sopparjok, Finnmark, Norway	Crd-grt-gneiss [CG]
26539	Cordierite Aust-agder, Norway	Crd-grt-bt-gneiss [CG]
TA-5	Cordierite Orijärvi, Finland	Orthoamphibole-Gneiss; Qtz-plag-crd-bt-ilmaath±ged±cum±alm; 3Kb, 550-600°C (3, 26, 27); [CG]
89 V	Cordierite Ivalojoiki-Inarijärvi, Finland	Antextite; Qtz-kfs-plag-grt-crd-bt-sill-ilma-py-po-zrn-sp; 8.1 Kb, 855-861°C (28); [CG]
I3	Cordierite Airport Ivalo, Finland	Kfs-qtz-crd-grt-plag-bt-sill-rut-zrn; 6.2-7.2 Kb, 760-830°C (28); [CG]

Appendix A		Continued	
G-155a	Cordierite	Muzkol Complex, East Pamir, Tajikistan	Crystals in pegmatite “dike” in bt-gneiss; Crd-qtz-mic-ab-tur-grt-zrn-col-bt-cbri; 580-650°C (29); [CG]
S. India 1	Cordierite	Kerala; Khondatite belt, India	Pegmatite vein cutting Schist; Crd-qtz-feld-bt-gneiss (1, 30); [CG]
42/IA	Cordierite	Kiranur, South India	Crd xenocryst found as loose material from weathered lava; 5-7 Kb, 850±50°C (25, 31); [CG]
129875	Cordierite	Manik Ganga, Sri Lanka	Granulite facies; Grt-crd-sill-bt-plag-qtz; 5-6 Kb, 730±20°C (32, 33); [CG]
CTSiM	Cordierite	Tsihombe, South Madagascar	Bt [CG]
C006	Cordierite	Madagascar	Pegmatite; Kfs-ab-qtz-tur-ms-ap-grt [CG]
X-1	Cordierite	Reynolds Range, Australia	Bt (1); [CG]

Mineral abbreviations: albite (ab), almandine (alm), andalusite (and), anthophyllite (anth), apatite (ap), beryl (brl), biotite (bt), chalcopyrite (ccp), chrysoberyl (cbrl), columbite (col), cordierite (crd), corundum (crn), cummingtonite (cum), garnet (grt), feldspar (fds), gedrite (ged), ilmenite (ilm), K-feldspar (kfs), kyanite (ky), microcline (mic), muscovite (ms), plagioclase (plag), pyrite (py), pyrrhotite (po), quartz (qtz), rutile (rt), sapphirine (sapp), sillimanite (sill), spinel (sp), staurolite (st), tourmaline (tur), zircon (zm).

Literature: (1) Vry et al. (1990), (2) Newhouse and Hagener (1949), (3) Iiyima (1960), (4) Leake (1960), (5) Barker (1962), (6) Mezger et al. (unpublished manuscript), (7) Pan and Fleet (1995), (8) Goldman et al. (1977), (9) James et al. (1978), (10) Robinson et al. (1986), (11) Robinson and Jaffe (1969), (12) Heinrich (1950), (13) Miyashiro (1957), (14) Newton (1966), (15) Povondra and Cech (1978), (16) Armbruster and Irouschek (1983), (17) Armbruster (1986), (18) Cesare et al. (1997), (19) Cesare (2000), (20) Cesare et al. (2007), (21) Schenk (1989), (22) Cerny et al. (1997), (23) Stanek and Miskovsky (1964), (24) Hochella et al. (1979), (25) Geiger et al. (2000), (26) Visser and Senior (1991), (27) Schneiderman and Tracy (1991), (28) Hörmann et al. (1980), (29) Stolpovskaya et al. (1998), (30) Chacko et al. (1987), (31) Lal et al. (1984), (32) Dahanayake (1980), (33) Malcherek et al., (2001)

Donors: [AMNH] – American Museum of Natural History, [KL] – Kristin Lazzeri [CG] – Charles Geiger

Appendix B		Electron-microprobe analyses (wt% oxides) of selected cordierite samples													
		C004**	26230**	TUB-1**	G-155a**	88593**	S. India	1*NE86A-248*	CL-177-1*	Geco Mine*	WYO-2*	Wards*			
SiO ₂	49.68	48.36	45.79	49.62	48.49	47.8	47.99	48.4	49.02	49.68	48				
Al ₂ O ₃	33.13	30.94	31.93	33.3	31.2	32.42	32.55	33.1	33.1	33.35	31.91				
FeO	2.29	6.24	16.22	2.62	6.79	7.32	7.97	5.69	4.6	2.53	5.6				
MgO	12.09	8.72	2.18	12.4	8.59	9.2	8.54	10.38	10.53	12.19	10.31				
MnO	0.05	0.43	0.7	0.04	0.38	0.05	0.05	0.06	0.22	0.05	0.05				
ZnO	tr.	n.a.	tr.	tr.	0.02	n.a.	n.a.	n.a.	0.07	tr.	n.a.				
CaO	0.03	b.d.l.	0.04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.02				
K ₂ O	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.08	0.03	0.02	b.d.l.	b.d.l.	0.02				
Na ₂ O	0.51	1.4	0.55	0.43	1.36	0.08	0.11	0.08	0.28	0.3	0.37				
H ₂ O	1.47	2.34	1.67	1.46	2.25	0.56	0.56	0.8	1.29	1.21	1.73 ^a				
CO ₂	0.66	n.a.	0.14	0.2	n.a.	0.88	1.37	1.11	1.25	0.51	0.82				
Total	100.03	98.44	99.32	100.08	100.06	98.39	99.17	99.64	100.4	99.82	96.21				
Si	5.004	5.08	4.958	4.991	5	4.976	4.991	4.962	4.994	4.997	5.002				
Al	3.933	3.831	4.075	3.932	3.791	3.977	3.99	3.996	3.974	3.953	3.919				
Fe	0.193	0.548	1.469	0.219	0.585	0.637	0.693	0.487	0.392	0.213	0.488				
Mg	1.816	1.366	0.351	1.851	1.32	1.428	1.324	1.585	1.599	1.827	1.601				
Mn	0.004	0.038	0.064	0.003	0.034	0.004	0.004	0.005	0.019	0.004	0.005				
Zn	tr.	n.a.	tr.	tr.	0.001	n.a.	n.a.	n.a.	0.005	tr.	n.a.				
Na	0.099	0.286	0.115	0.083	0.27	0.016	0.021	0.016	0.056	0.058	0.041				
K	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.01	0.004	0.002	b.d.l.	b.d.l.	0.003				
Ca	0.003	b.d.l.	0.004	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.002				

* Data from Vry et al. (1990) - Chemical formulas normalized to 18 oxygens.

** Data from Bertoldi et al. (2004) - If both SIMS and ICP-MS data are available, the latter had been used for the calculation of the chemical formula. The chemical formulae of cordierites were calculated on the basis of 36 positive charges.

Appendix B Continued		C ^T SiM*: H06** 106886* VS-1** TA-5** 42/IA** 118171* 7114** 129875* C006 **											
SiO ₂	49.67	47.71	49.47	48.75	49.28	49.65	49.1	48.67	49.76	49.62			
Al ₂ O ₃	33.31	32.15	33.01	32.94	33.13	33.17	33.01	32.8	33.6	33.32			
FeO	2.57	12.2	1.27	6.41	4.26	2.34	3.73	6.58	1.06	2.63			
MgO	12.15	5.47	12.86	9.44	10.97	12.54	11.13	9.44	12.99	11.99			
MnO	0.02	0.67	tr.	0.07	0.09	0.03	0.34	0.04	tr.	tr.			
ZnO	<i>tr.</i>	<i>0.01</i>	<i>tr.</i>	<i>0.02</i>	<i>0.1</i>	<i>tr.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>tr.</i>	<i>tr.</i>			
CaO	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
K ₂ O	0.02	0.14	<i>b.d.l.</i>	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.04	b.d.l.			
Na ₂ O	0.02	0.2	0.32	0.11	0.25	0.33	0.38	0.09	0.15	0.18			
H ₂ O	1.15	0.37	n.a.	0.75	2.06	1.21	n.a.	0.26	0.38	1.12			
CO ₂	0.9	0.28	n.a.	1.32	0.2	0.59	n.a.	1.23	1.74	1.02			
Total	100.01	99.35	96.94	99.82	100.3	99.85	97.73	99.14	99.73	99.89			
Si	5.002	4.998	5.007	5.003	4.997	4.99	4.993	5.004	4.993	5.006			
Al	3.954	3.954	3.937	3.984	3.958	3.935	3.965	3.978	3.974	3.962			
Fe	0.216	1.069	0.107	0.55	0.361	0.197	0.317	0.565	0.089	0.222			
Mg	1.825	0.854	1.94	1.445	1.658	1.866	1.688	1.447	1.943	1.803			
Mn	0.001	0.059	tr.	0.006	0.008	0.003	0.029	0.003	tr.	tr.			
Zn	tr.	0.001	tr.	0.001	0.008	tr.	n.a.	n.a.	tr.	tr.			
Na	0.04	0.041	0.064	0.023	0.05	0.064	0.076	0.019	0.029	0.034			
K	0.003	0.019	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.05	b.d.l.			
Ca	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			

b.d.l. = below detection limit

tr. = trace amounts

n.a. = not analyzed

Italic numbers = values obtained by ICP-MS

^a = Uneven IR spectral baseline in H₂O stretching region, IR H₂O determinations uncertain

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